



280282

Remedial Investigation/ Feasibility Study

Crab Orchard National Wildlife Refuge

U.S. Fish and Wildlife Service
U.S. Department of Interior
Marion, Illinois
and
Sangano-Weston, Inc.
Atlanta, Georgia

September 1986



O'BRIEN & GERE

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September 3, 1986

Mr. Dick Ruelle
Resource Contaminants Assessment Coordinator
U.S. FISH AND WILDLIFE SERVICE
1830 Second Avenue
Rock Island, Illinois 61201

Re: Crab Orchard RI/FS Quality
Assurance Project Plan

File: 3114.001

Dear Mr. Ruelle:

On July 23, 1986, we received U.S. EPA's comments to our revised QAPP which was submitted on May 28, 1986. The comments were discussed in detail at a subsequent meeting between O'Brien & Gere, Fish & Wildlife Service and U.S. EPA in Chicago on August 11-12, 1986. Enclosed is a copy of the Quality Assurance Project Plan, Revision 2. Indicated below is a summary of responses or changes which have been incorporated into the revised Quality Assurance Project Plan. The comments are enumerated in the sequence which accompanied Mr. Boice's letter of July 21, 1986.

- 0.) Rewriting the QAPP to include only Phase II would dilute the clarity of understanding of the overall program. We have therefore added a qualifier to Section 1, page 1 which states that Phase I sampling and analysis has been completed and that the Phase I information is presented for informational purposes only. We have also noted that U.S. EPA approval of the QAPP applies only to Phase II activities proposed in the Work Plan Supplement - Phase II Site Operations Plan, Sept. 1986.
- 1 1.) Section 1.04, Table 2 has been modified to Tables 2a and 2b to include specific parameters which accompany each Phase, while Table 2c provides a list of compounds analyzed under each of the parameters. More details on sampling and analysis by sites and sample types are presented in Tables 5 and 6 for Phase I and in Table 7 for Phase II. Note that Table 7 has been completely revised to show specific parameters for specific sample types without the use of analysis sets.
- 1 2.) It is not typical practice to analyze unfiltered samples on well waters. It is less expensive to run both filtered and unfiltered

metals on groundwater rather than going back to resample. We have therefore revised Section 1.06, Table 7 to include both filtered and unfiltered metals. A footnote has also been added to Section 5, Table 10 at page 5 specifying the filtration protocol. Section 4.05, page 8 has been modified to specify that well waters will be filtered in the field and the filtration protocol included therein.

- I 3.) Section 1.04, page 26 has been modified to specify the fish compositing procedure and the fish portion (skin-on fillets). Percent lipids has been added to fish analysis. Section 5, Table 10 at page 18 has been modified to include the methodology for percent lipids. Procedures from the USFWS call for skin-on fillets for carp and bass, and skin-off fillets for catfish and bullhead.
- I 4.) Section 4.03, page 2 has been modified to describe the compositing procedure to be used for the water sampling locations at Site 34 Crab Orchard Lake. A composite water column has been specified because the eastern portion of the lake is very shallow and not expected to be significantly stratified.
- I 5.) Subsequent to discussions and agreements between Boice, Ruelle, and O'Brien & Gere during the August 11-12, 1986 meeting on the Phase II Site Operations Plan, Tables 4, 5, 6, and 7 have been modified to reflect agreed changes.
- I 6.) Section 1.04, page 18 has been modified to indicate that an additional objective of the RIFS is to determine the most cost effective remedial actions. The list of remedial actions in Section 1, page 18 has been modified to include incineration of soil.
- I 7.) The inconsistencies on Tables 4 through 7 appear to be due to the fact that there are several samples that are scheduled as part of Phase I but will be collected and analyzed (e.g. well water, lake water and sediments) in Phase II or were collected in Phase I (e.g. lake fish) for analysis in Phase II. These inconsistencies have been corrected.

Table 4 now provides a summary of sampling and analysis completed for Phase I using the analysis sets defined in Table 5 and list of Phase I analysis by site and sample type in Table 6. Table 7 now presents in detail all analyses by site, sample type and parameters in Phase II, including groundwater and biota.

- II 1.) Section 2, page 1 has been modified to provide clarification of the functional management responsibilities of the Fish and Wildlife Service and U.S. EPA. As a general guideline, EPA will provide

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oversight as it relates to human health, while FWS oversight relates to impacts on wildlife.

- II 2.) Section 2, Table 8 has been modified to specify laboratories used for analysis, while specific analysis to be performed by these laboratories are identified in Section 2, page 4.
- II 3.) Per earlier discussions, it had been agreed that the Refuge Manager would be the community relations contact.
- II 4.) Section 2, Figure 3 has been modified to include David Payne as U.S. EPA's Quality Assurance Manager.
- II 5.) Section 2 have been modified to identify the specific persons who will perform the following tasks:
 - performance and system audits
 - supplying performance evaluation samples
 - data corrective action
 - risk assessment
 - lab custody
- III.) Section 3, Table 10 includes the QA/QC objectives specified for EPA's Contract Laboratories program. In most cases, the actual quality control values produced by the laboratories' methods and instruments are superior to the QA/QC objectives. The stated CLP objectives are still valid in these cases. Deviations from the stated detection limits are often caused by matrix interferences where the presence of one compound at high concentrations interferes with the detection limits for other compounds. It is not possible to anticipate these effects in the detection limits. Such interferences are noted on the analytical reports.
- IV 1.) As discussed under Item 0, a qualifier has been added to Section 1, page 1 which states that the Phase I information is presented for informational purposes only and that U.S. EPA approval of the QAPP applies only to the Phase II activities.
- IV 2.) Split spoons were used to collect soil and sediment core samples, and is anticipated to be used instead of lexan coring device. Section 4, page 3 has been modified.
- IV 3.) Section 4, page 3 has been revised to describe soil and sediment sampling by methods other than split spoons.
- IV 4.) Section 4, page 5 and Table 4 have been modified to include the method for aquifer slug tests.

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- IV 5.) All references to peristaltic pumps have been removed from Section 4.
- IV 6.) Section 4, page 8 has been modified to include specification for field filtration of all ground water samples for metals and Table 10, page 5 has been modified to include filtration procedure.
- IV 7.) The discussion of sampling equipment at Section 4, page 4 has been modified to include additional information about sampling equipment which has been taken from the Phase II Site Operations Plan. This material has been added in Attachment 4.
- IV 8.) The reference to NEIC's guidance documents in Section 4, page 15 is accurate as given. The wording has been changed to say Revised 1985 edition.
- IV 9.) The reference to decontamination protocols in Section 4, page 4 has been changed to refer to text on pages 9 to 11 of Section 4.
- IV 10.) Procedures for monitoring well installation have been added to Section 4 at page 6.
- IV 11.) Section 4, page 5 has been modified to specify sampling equipment which is dedicated to use at one spot and equipment which is decontaminated between uses.
- IV 12.) Sample containers and preservatives have been included in Section 4, page 15. The reference to packing and labelling procedures has been changed in Section 4, page 21 to the Site Sampling Plan, June 1985.
- IV 13.) Nine PVC ground water monitoring wells were installed during Phase I in accordance with the procedures provided in the Work Plan dated June 1985. Since the major contaminant issues at the Refuge are PCBs and heavy metals, we do not see that PVC well construction is inappropriate. However, additional wells installed during Phase II will have PVC casing and stainless steel screens.
- VII 1.) Section 7, Table 10 has been modified to specify the method which applies to a particular analysis scheduled for Phase II only.
- VII 2.) Pages 3 through 6 of Section 7 represent Phase I screening procedures and have been deleted. A Standard Operating Procedure (SOP) has been developed in Section 7 to describe the PCB extraction procedure which deviates from CLP procedures. The mercury detection limits in the Phase I analyses were higher than

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CLP limits because of interference from chlorine gas in the digestion step. The problem has now been corrected.

- VII 3.) Additional information on the analytical methods for biota have been included in Table 10, Section 7. In addition, a SOP describing the fish preparation procedures has been included as Attachment 3.
- VII 4.) The scanning procedures which are described on pages 3 to 6 of Section 7 were used only in Phase I and have been deleted.
- VII 5.) Some of the detection limits for flame atomic absorption have been changed on Table 10 of Section 7.
- VII 6.) No metals are being analyzed by the ICP procedure in Phase II.
- VIII 1.) The EPA guidance materials which we were provided specified that Sections 8 and 12 should be separate sections. In the revised Sections 8 and 12, we distinguish that the data reduction, validation and reporting (Section 8) are functions performed by O'Brien & Gere, while data assessment (Section 12) is a function provided by FWS and EPA.
- VIII 2.) Data assessment procedures and functions are addressed in the revised Section 12. Additional details on data reduction, validation and reporting have been added to Section 8.
- IX 1.) QC audits and acceptance criteria are included in Table 10.
- IX 2.) The discussion of sample containers, blanks, preservatives and field procedures has been moved to pages 15 of Section 4.
- IX 3.) On page 1 of Section 9, the discussion of matrix spikes has been changed to reflect spiked sample analysis.
- IX 4.) The reference to Attachment 4 has been deleted.
- X 1.) Specific audit duties have been added to Section 10.
- X 2.) A systems audit by Region V QAO was on August 20-21, 1986 to cover Phase II methods and procedures.
- XII 1.) As previously stated under item VIII 1), we disagree that this Section should be combined with Section 8.

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- XII 2.) The text of Section 12 has been revised to reflect the activities which will be conducted by EPA and FWS in performing data assessments.
- XIII 1.) The reference to Attachment 4 on page 1 of Section 13 has been deleted.
- XIV 1.) Quarterly performance evaluation samples are inappropriate for this project. The Phase II sampling and analysis is a one-time event which will be completed within a period of eight weeks. Hence, one set of performance evaluation samples is scheduled prior to initiation of Phase II.
- XIV 2.) Five water supply samples from Crab Orchard Refuge and the City of Marion were analyzed for primary and secondary drinking water parameters as part of Phase I. These preliminary results were reported in Status Report No. 4 dated January 10, 1986. The five water samples have been scheduled for additional analysis in Phase II.

Responses to the Comments on the April 1986 Work Plan Supplement will be submitted as part of a separate letter with the revised Work Plan Supplement - Phase II Site Operations Plan on September 10, 1986. Please contact me if you have any questions on the materials presented here.

Very truly yours,

O'BRIEN & GERE ENGINEERS, INC.


Cornelius B. Murphy, Jr.
Senior Vice President

Encl.

cc: Mr. Richard Boice (U.S. EPA) (4 copies)
Mr. John Hanson (Beveridge and Diamond)
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QUALITY ASSURANCE PROJECT PLAN (QAPP)

REMEDIAL INVESTIGATION/
FEASIBILITY STUDY
CRAB ORCHARD NATIONAL WILDLIFE REFUGE

U.S. FISH AND WILDLIFE SERVICE
U.S. DEPARTMENT OF INTERIOR
MARION, ILLINOIS
AND
SANGAMO-WESTON, INC.
ATLANTA, GEORGIA

SEPTEMBER, 1986

O'BRIEN & GERE ENGINEERS, INC.
1304 BUCKLEY ROAD
SYRACUSE, NEW YORK 13221

REMEDIAL INVESTIGATION/FEASIBILITY STUDY
(RI/FS)

REVISED QUALITY ASSURANCE PROJECT PLAN

Project Title: Crab Orchard National Wildlife Refuge
EPA Project Officer: Richard Boice

Prepared by: O'Brien & Gere Engineers, Inc.

Date: 9/2/86

Approved: *Richard Boice*
O'Brien & Gere Engineers, Inc.
Project Officer

Date: 9/2/86

Approved: _____
OBC Laboratories, Inc. Manager

Date: _____

Approved: _____
FWS Project Manager

Date: _____

Approved: _____
EPA Remedial Site Project Manager

Date: _____

Approved: _____
EPA QA Officer

Date: _____

Dave:

See me and sign this form.

ETC

Rocky Mountain Laboratories

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2. RI/FS Work Plan (June 1985)
3. Work Plan Supplement - Phase I (Dec. 1985)
4. Work Plan Supplement - Phase II (Sept. 1986)

*Not included in
Phase II*
*these are
not at
Site 34*

SECTION 1 - PROJECT DESCRIPTION

1.01 Introduction

O'Brien & Gere Engineers, Inc., is currently responsible for a Remedial Investigation/Feasibility Study (RI/FS) at the Crab Orchard National Wildlife Refuge in Marion Township, Williamson County, southern Illinois. Information obtained from previous studies and historic information provided by the Refuge Manager; lead to the selection of 31 sites within the Crab Orchard National Wildlife Refuge for investigation. Two additional sites were also included to serve as background or control sites.

In order to direct and control a multi-sited investigation representing various matrices (soil, sediment, water, biota, etc.) it was determined that the study be conducted in 2 phases.

The objective of Phase 1 was to identify, through a qualitative approach, ^{he}~~whether~~ ~~sa~~ contamination was present on a given site and to define the range of chemical compounds which contributed to the problem.

The Phase 1 sampling and analysis program was initiated in July 1985 and completed in November 1985. Phase 1 references and data are included in this QAPP for background information only, consequently they are not presented as items for EPA approval.

As required by the Environmental Protection Agency (EPA), a Quality Assurance Project Plan (QAPP) has been prepared for Phase II of this RI/FS and is presented herein.

At the conclusions of Phase 1 analytical results of the 500 plus samples were reviewed and 16 sites were selected for Phase 2 sampling. The selected Phase 2 sites will not receive a quantitative approach. The 16 selected sites will receive a comprehensive evaluation, horizontal and vertical, of the compounds identified in Phase 1. The information generated during Phase 2 will be used to complete the feasibility study.

This QAPP includes, in specific terms, the policies, organization, objectives, activities and specific Quality Assurance (QA) and Quality Control (QC) activities designed to achieve the data quality goals of this project. Where possible, existing QA/QC guidelines, policies, programs, etc., are incorporated into the QAPP by reference.

The purposes of this remedial investigation are: 1) to determine the nature and extent of any contaminant problem at several sites (Table 1) located around the eastern section of the Crab Orchard Lake (Figure 1) on the Crab Orchard National Wildlife Refuge and tributaries that drain into Crab Orchard Lake and 2) to gather all data necessary to support the Feasibility Study. This will involve the following activities:

*Present plan
appears
insufficient to
confidently define
these.*

- Determine current groundwater gradients.
- Determine the extent of groundwater contamination that has occurred and the rate and direction of contaminant migration.
- Assess levels of contaminated soil that may be present adjacent to disposal areas.
- Identify the areal extent of disposal areas.
- Identify specific contaminants which may pose acute or chronic hazards to public health, welfare or the environment.

- Identify pathways of contaminant migration from the sites.
- Define on-site physical features and facilities that could affect contaminant migration, containment, or cleanup.

O'Brien & Gere will furnish all personnel, materials and services necessary for or incidental to performing the remedial investigation on the Crab Orchard National Wildlife Refuge.

The remedial investigation consists of eight tasks:

Task 1 - Description of Current Situation

Task 2 - Investigation Support

Task 3 - Site Investigation

Task 4 - Preliminary Remedial Technologies

Task 5 - Site Investigations Analyses

Task 6 - Final Report

Task 7 - Community Relations

Task 9 - Additional Requirements

1.02 Site Location and History

Crab Orchard National Wildlife Refuge (CONWR or the Refuge) is located in southern Illinois primarily within Williamson County, but also extends into neighboring Jackson, Union and Johnson Counties. There are twelve lakes located within the Refuge including Crab Orchard Lake. Crab Orchard lake was completed in 1940 and has a surface area of 6,965 acres, a maximum depth of 30 feet and 635 acre-feet of storage capacity. The watershed drainage area is 109,261 acres. In addition to supporting an active sport fishing population, the lake serves as water supply (approx. 280,000 gallons per day) for the Refuge and

Federal Penitentiary located southeast of the Refuge. The City of Marion has a supplemental water intake in the Lake which has rarely been used.

The Refuge is administered by the U.S. Fish and Wildlife Service (FWS) of the Department of the Interior (DOI). During the early 1940s and continuing to the present, a number of industries have been active on the Refuge. Industrial activity was especially heavy during World War II when as many as 10,000 persons were employed by a number of defense-related industries. The section of the Refuge containing the industrial facilities lies within the eastern drainage area for the Crab Orchard Lake. The western portion of the lake has been used primarily for recreational purposes.

These industrial facilities were involved in a variety of manufacturing processes such as:

- Manufacture of land mines and bombs
- A munitions plant
- Manufacture of printing inks
- Production of radio speakers
- Metal plating, painting, metal work electrical work

To support these facilities, industrial dumps were developed within the Refuge. During the early 1940s, too, the Crab Orchard site was repeatedly sprayed with lead arsenate to control insects.

From the late 1970s through the present, sampling has been conducted to permit analysis of contamination. Until 1981, the main parameters of interest were lead, mercury, and other heavy metals, notably

cadmium. After 1981, analyses were conducted also for PCBs, dioxins, and benzo furans.

Phase I of the Remedial Investigation encompassed thirty-three (33) sites, including two control sites. The histories of each site are as follows:

Site 3: Area 11 South Landfill

Areas 11 and 12 are currently abandoned sites of explosives and nitrogen fertilizer manufacturing as well as munitions loading. The Olin Corporation is reported to have operated a dynamite line there which was later reportedly sold to U.S. Powder. A number of fires and explosions are known to have occurred in these areas. Use of lead azide in the area is suspected. RDX may have been used in this area. Many of the buildings and grounds have been "torched" to remove residuals of flammable material. Most of the buildings are covered with a spark-retarding asbestos siding material. Also, within Area 11 are storage areas where explosive powders were stored in rubber-lined underground trenches. A burning pad is evident to the south of Area 11 where oil residues, 50-calibre powder magazines and small powder cylinders are noticeable on the surface. The evaluations of these areas are not included in this scope of work. *Is this a separate area? If so what is the limit?*

The Area 11 South Landfill is located adjacent to what appears to be an old railroad bed. Much surface and buried litter is evident over an area of perhaps 10 acres. In addition to railroad track, ties and ballast, the following were also observed: cinders and charred wood, powder canisters, piping, metal, mesh, bricks, pumice blocks, 30- and

55-gal drums, reinforcing bars, a laboratory flask and miscellaneous wire and plastic articles. One mound on the bank just above the stream bed has several of what appeared to be metal vents on the top and a 4-in stainless steel pipe drain extending from the bottom. The stream bed west of the road appeared to contain especially heavy concentrations of debris. Black tars and ash were evident in the stream bed.

*Is this or is this not a landfill?
If it is a landfill, what is it?
There,*

Site 4: Area 11 North Landfill

The Area 11 North Landfill appears to have been the site of a large (2 to 3 acre) impoundment. The impoundment is flat in the middle and has small intermittent stream or marsh areas bordering the east and west boundaries. Water appears to flow from south to north following periods of precipitation. The reinforced concrete remains of a dam can be seen at the northwest end of the site. A large earth bunker is located immediately to the west. It may have been built with earth excavated from the semi-marshy lagoon area and may have been constructed to protect the explosives processing areas located further to the west. It was suggested that RDX or magnesium may have been stored underwater here or the area may have been used to detonate explosives or for experimental detonations. The level bottom of the impoundment shows a number of bare patches of fine white silt or clay. Other weathered areas showed horizontal layering of white and gray sediments. A number of dynamite-type fuses were noticed here as well as a small powder carrier, 1.5-in dia by 3 in, with the fuse intact. Small lead chunks were also observed.

Site 5: Area 11 Acid Pond

The Area 11 Acid Pond is a diked impoundment approximately 300 ft x 150 ft which received drainage flowing north from the Area 11 process buildings. The dike extends 5 to 6 ft above the current water level. A 12 inch diameter pipe exits to the west through the levee to a valve box which controls the discharge from the pond to a small stream. This drainage then exits through the woods and swampy areas to the north. It is claimed that a spill of low-pH water (nitric acid) from the pond years ago killed all of the downstream vegetation for 1/4 mile. A large stand of dead trees is still visible along the creek north of the pond.

Sites 7, 8, 9, 10 and 11

D AREA SOUTHEAST DRAINAGE

D AREA SOUTHWEST DRAINAGE

P AREA NORTHWEST DRAINAGE

WATERWORKS NORTH DRAINAGE

P AREA SOUTHEAST DRAINAGE

The Olin D and P Areas are active Olin operations north of Crab Orchard Lake. Explosives are currently manufactured in the D Area while research and development is conducted in the P Area. It is likely that chemicals handled in the P Area are non-conventional or "exotic". Universal Match also previously conducted operations here under contract to the DOD. Their operations ceased after a large explosion.

Sites 7, 8, 9, 10 and 11 are locations within various drainage channels leading from the Olin D and P Areas. These discharge to the Lake near the Refuge Waterworks.

Site 7A:D Area North Lawn

There is a large (about 3 acre) lawn located northwest of the active Olin D Area complex. It is claimed that barrels of chemicals were dumped on a knoll within this lawn. No evidence of a knoll was seen during the site visit, but a number (about 8) of depressed brown patches were evident on the lawn. A visually clean drainage channel is located south of the lawn and exits under the fence to the west. Other moist drainage areas extend to the wooded area to the west of the site.

Site 11A: P Area North

Located outside of the fence north of the Olin P Area is an abandoned L-shaped loading area with connecting covered walkways approximately 100 ft and 85 ft. The central structure contains a loading dock and a steamhouse containing a concrete pit with about 5 ft of clear standing water. An old roadbed runs west and north of the structure and draining swales surround all of the buildings. An abandoned (?) sewer line also runs across the north edge of the site. It has been reported that contaminants were dumped on the ground outside of the building.

*There was a lot of things
what was sampled was the impoundment.
Therefore was the landfill really investigated?
Should it be?*

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Site 12: Area 14 Landfill

Area 14 was a site of munitions loading activity. Many of the buildings have been abandoned or demolished, but a few industries presently occupy some of the buildings. Historic aerial photos indicated what appeared to be landfill activity in the field east of the presently-occupied buildings. During the site visit the remains of a 100-ft dia circular impoundment were found at this site. The interior of the impoundment is presently overgrown with trees with trunk diameters of 8 to 10 in, indicating the date of the impoundment closure at about 1955 to 1965. The impoundment walls are about 6 ft high and the north wall has been breached to allow drainage to flow from the impoundment to an adjoining field. Several black oily pools are evident within and outside the basin. Other bare patches of black sediment and tars are located around the basin floor.

Site 13: Area 14 Change House Site

Southeast of the active Diagraph-Bradley buildings on Area 14 was an old building which was recently demolished. Formerly, it was the site of a "Change House" where workers changed their clothing after working in the adjacent bomb-loading buildings. At one time a company named CTI (Chemicals and Technology, Inc.??) manufactured explosives and other chemicals in this building. Other industries may also have occupied this building. The change building was supposedly located across from the bomb-loading building on a plot of land just southeast of the intersection of two roads on the north edge of a big dirt mound. The concrete floor of the change house is under this mound. Aerial photos show another building (no longer present) further east of the

corner; field inspection revealed several 1/2-in reinforcing rods imbedded in concrete near the corners of this building.

Site 14: Area 14 Solvent Storage

Diagraph-Bradley or Diagraph Marking Systems currently operates within a complex of buildings in Area 14. They produce inks, stencils, stencilboards and marking pens. Linseed oil and various solvents are handled in bulk and in drums here. Some of the bulk solvents noted were: T25 Xylene, T8 Diacetone Alcohol, T9 Diethylene Glycol, and T18 Methyl Cellosolve. Several compressed gas cylinders are also present. At least two drum storage areas containing 50 to 200 drums were also noted. Spill containment facilities are minimal. A drainage ditch runs north parallel to the road west of the buildings. Process water from the Diagraph-Bradley buildings enters this ditch from a standpipe.

Sites 15 and 16

AREA 7 PLATING POND

AREA 7 INDUSTRIAL SITE

Area 7 contains a complex of 33 identical buildings which have been used for a variety of industrial purposes during the past 40 years. Each of the six rows of buildings was previously served by a railroad siding.

Within a wooded rise to the south is located a small pond (approximately 50 ft x 30 ft) which is bermed about five ft above the current water level. The current water depth is estimated to be about four ft.

It is claimed that this pond was used to receive plating wastewaters from Olin operations which were located in this area at one time. PCBs, lead and other heavy metals may be of concern here.

Many of the buildings on the Area 7 site are used for dry warehousing purposes. However, two specific locations have been specified for sampling. Buildings 3-4, 3-5, and 4-4 are used by Pennzoil for waste oil recovery and recycling operations. Black residues are noticeable around some of these buildings. Buildings 5-2 and 5-3 are used by a refurbisher of mining machinery. Black residues are also evident around these buildings. A drainage channel runs from south to north through the center of the site.

Site 17: Job Corps Landfill

Northeast of the Refuge Waterworks is a small (approximately 10 acre) pond created by Job Corps workers in the mid-1960's. Attention has recently been brought to this pond because as many as thirty or more geese carcasses have been found floating on the water or littering the shores. Some of these carcasses have been relatively fresh while others were in various state of decay. The Fish and Wildlife Service has completed extensive analyses of these carcasses and has ruled out a variety of potential chemical causes. A definite conclusion has not yet been reached.

The "Job Corps" landfill was discovered while investigating the geese kills. It is located within a wooded area to the north and adjoining the pond and covers an area of perhaps an acre or more. It appears to be mainly surface litter dumped in spots and perhaps spread

around, although deeper spots cannot be ruled out. Many of the surface articles appear to be connected with food preparation, e.g. institutional-size food cans, and a variety of bottles. The bottle styles and labels suggest a date of the mid-1950's, which was consistent with a 1956 Illinois automobile license plate also found. Many of the debris piles are overgrown by thick brush. Two bare patches (less than 6-ft diameter each) were located among the debris. Mica flakes and small electrical contacts were found in one of these. It is claimed that small electrical capacitors were also found here, but none were noted during this site visit. Probing with a trowel revealed no further debris beneath the top inch of soil.

Site 18: Area 13 Loading Platform

On the northwest end of the Area 13 munitions storage bunkers is a concrete loading platform adjacent to the abandoned and dismantled rail line. It is reported that munitions-type chemicals were dumped off the platform. The site inspection indicated that the elevated concrete loading dock is about 235 ft long by 10 ft wide and about 5 ft high. The dock is supported on concrete posts spaced 9 ft apart. The northwest side contains stone bedding (probably from the oil railroad bed) with a number of small areas of ponded water. No unusual vegetation changes were detected. The only unusual item was a pile of dirt and stone rubble off the west end of the dock with a rusted drum shell nearby.

Site 19: Area 13 Bunker 1-3

Area 13 contains approximately 85 bunkers which were originally built for storage of 500-lb bombs. Most of them still contain explosives, leased mainly to Olin and U.S. Powder. Agricultural fields are cultivated between the bunkers. Formerly, they were fruit orchards.

It has been reported that chemicals were poured out near Bunker 1-3, probably in the field next to it. A site inspection did not reveal any significant signs of impact. Evidence of fill activity (scattered red bricks) is widespread. An L-shaped area of brown vegetation difference was noted to the west side of the bunker.

Site 20: D Area South

An abandoned building is located within the fenced southeastern end of the Olin D Complex. It was reported that chemicals were dumped here. A drainage swale originating at the building runs east outside of the fence. A four-in pipe (dripping) extends from the Olin Area under the fence and discharges to this ditch. A slight sheen was noticeable on the surface water in pooled areas of the ditch.

Site 21: Southeast Corner Field

At the southeast corner of the refuge is a field which is thought to be the site of a very old landfill. A pile of concrete pieces, possibly from an old bridge, is located immediately inside the fence. The topography gradually slopes to the south and east with a swampy drainage ditch at the bottom of the slope. No other evidence of debris could be found. Trees as large as 24-in in diameter suggest that the

area has not seen any soil-disturbing activity within the past 60 to 70 years.

Site 22: Old Refuge Shop

North of the refuge along Wolf Creek Road is the old refuge headquarters, now leased by Diagraph Bradley. Behind this building is located the old shop area of the refuge. Pine poles were treated here with pentachlorophenol and shipped to various spots around the country. Outside the fence to the north is a small pool which receives drainage from the old shop area. The pool contains a green-yellow scum and drains through the woods to the northwest.

Site 24: Pepsi-West

The Pepsi Cola Bottling Company in Marion could potentially discharge to Crab Orchard Creek. It is not known whether the City or State monitor environmental activities here. A site inspection indicated that it was unlikely that discharges issued directly south to the Creek, since the entire south end of the property rises 4 to 8 ft in elevation above the parking lot. Drainage ditches, however, were located to the north adjacent to the street. These probably receive surface runoff only.

Site 25: Crab Orchard Creek at Marion Landfill

The old Marion landfill is off Old Creal Springs Road and directly abuts Crab Orchard Creek. It has apparently been inactive for a number of years. A visible face of trash can be seen by travelling

upstream several hundred yards from the road. Near to this is a small pond (approximately 3/4 acre).

Sites 26 and 27:

CRAB ORCHARD CREEK BELOW MARION STP

CRAB ORCHARD CREEK BELOW 157 DREDGE AREA

The Marion sewage treatment plant discharges to Crab Orchard Creek somewhere upstream of Court Street. A number of samples downstream from the Marion STP are scheduled to assess the quality of various stretches of Crab Orchard Creek.

Site 28: Water Tower Landfill

Aerial photos indicate landfilling activities adjacent to the water tower near Areas 7 and 14. These activities are not visually apparent today. The sloping face northeast of the water tower is heavily overgrown with briars and rutted with several major gullies. Only a small amount of refuse is evident on this slope. A previous soil sample taken in this area showed 800 ppm lead concentration. More activity is evident in the woods at the bottom of the slope. A number of rusted drums, metal parts and tar residues can be found here. Standing water in the main drainage gully shows a slight sheen on the surface. Several small mounds are within the woods and a larger mound is located at the top of the hill.

Site 29: Fire Station Landfill

Located southwest of the refuge fire station is a large field which was used for storage of mining machinery until several years ago. The northern and western edges of this field show evidence of a large dump site. Debris is evident on the face which drops 4-5 ft. to a swampy area to the west. Previous sampling near an evergreen tree on the north side showed lead concentrations of 553 ppm. A slight sheen is noted in spots within the swamp. Most of the debris consists of concrete, metal, wire and other machinery-related items. It was reported that Olin dumped heavily here and there once was a very hot fire. Ignitable magnesium is suspected to be in the fill. An empty 30-gal drum labelled "Magnesium Powder" was found along the south portion of the eastern face.

Site 30: Munition Control Site

A munition control site is established on an area where the operations involved only ammunitions manufacture.

Site 31: Refuge Control Site

A control sampling station is established on an uncontaminated area of the refuge behind the new Refuge headquarters. Selection of the control site was coordinated with the Refuge Manager, following a site visit.

Site 32: Area 9 Landfill

The Area 9 Landfill was used during the 1950's and early sixties and was probably closed in 1964. The Landfill is located below

approximately 100 yds south of Crab Orchard Lake and approximately 100 yards east of the building complex. Runoff can drain from the landfill into an intermittent creek and then to the Lake. The limits of the landfill are discernible by changes in the topography and vegetation. It is approximately 2.5 acres with a fill thickness of 8 to 10 feet in the middle and 6 feet at the edges. Waste materials are exposed at locations where cover material has eroded. Some areas are void of vegetation.

The volume of the landfill is estimated to be from 16,000 to 35,000 cubic yards. Materials visible on the surface appear to be electrical components consisting of small capacitors, capacitor parts, large chunks of a golden resin, and a large number of 3-inch steel cuplike pieces.

Wastes were burned, compacted in a swale and covered when the landfill was active. Specific compounds of concern include lead, acetate, PCBs (Aroclor 1254 and 1242), and PCB burning products. Other possible materials from capacitor manufacturing include mica, silver, cyanide, aluminum hydroxide, aluminum oxide, gold, copper, zinc, hydrochloric acid, styrene, nitric acid, phosphoric acid, and borates. Other industrial wastes may include cyanides, printing inks and lead-based explosives. A magnetometer survey indicated a high concentration of metals on the east side of the landfill.

Site 33: Area 9 Building Complex

The Area 9 Building Complex was leased during the period from 1946 to 1962 as the Ordill Facility containing the Sangamo Capacitor Division. Manufacturing operations began in the early 1950's. This

division manufactured power factor capacitors, AC motor run capacitors, and a variety of DC capacitors. The components were of various types and included aluminum, electrolytes, mica, and silver and lead foil. The Division also manufactured small transformers that used mineral oil as a dielectric.

Subsequently, Olin Corporation started using the industrial facilities at the site. Olin manufactured explosives that were used to start jet engines. The company used nitro-glycerine in its operation.

Site 34: Crab Orchard Lake

Crab Orchard Lake (completed in 1940) has a surface area of 6,965 acres, a maximum depth of 30 feet, and 635 acre-feet of storage capacity. The watershed drainage area is 109,261 acres. The lake has a retention time of approximately 0.8 years. Water enters the lake through several creeks, including Crab Orchard Creek on the eastern end of the lake and an intermittent creek adjacent to the Area-9 Land-fill. Water leaves the lake through Crab Orchard Creek on the western end of the lake. In addition, 280,000 gallons/day of water is used by the Refuge.

The eastern section of the lake is near several manufacturing operations established since the 1940s.

1.03 Project Objectives

The primary objectives of the RI/FS are to determine any hazards to human health and the environment as well as to recommend the most cost-effective source control and off-site remedial actions. Source

control remedial actions include measure to prevent, reduce, or eliminate contamination either by containing the hazardous wastes in place or removing them from the site. Off-site remedial actions include measures to mitigate the effects of hazardous waste contamination that has migrated beyond the site. Appropriate source control and off-site remedial actions will be formulated and analyzed in detail after sufficient data have been generated through the remedial investigation.

Based upon existing data, remedial actions that may be appropriate for the CONWR site include, but are not limited to, one or a combination of the following:

- No action.
- Removal and disposal of waste material.
- Solidification or stabilization of waste material.
- In place reconstruction or encapsulation of waste material.
- Contaminated soil incineration.
- Continued off-site monitoring.
- Limit access to contaminated areas.
- Groundwater collection and treatment systems.
- Surface water drainage measures to prevent ponding on or near sites of contamination.
- Construction of groundwater barriers.
- Construction of a clay or synthetic cap over contaminated.

Presently, the available data and information on the site are insufficient to allow a definitive selection, screening, and feasibility study of remedial action alternative.

1.04 Project Description

The remedial investigation/feasibility study (RI/FS) for the Crab Orchard National Wildlife Refuge Site is intended to determine the nature and extent of contamination, to develop and evaluate remedial alternatives and to identify cost-effective remedial actions to be taken at contaminated sites on the refuge which reduce risks to acceptable levels. To accomplish this, the following tasks will be completed:

- characterize the on-site soil, sediment, water and biological samples for the presence of hazardous contaminants (includes landfill, surface soil, pond and lake water).
- identify pathways of chemical migration from the site.
- characterize the off-site soil, sediment, water and biological samples for key hazardous components.
- determine and describe on-site physical features that could affect migration of key hazardous components, methods of containment, or methods of remedial action clean-up.
- develop viable remedial action alternatives.
- permit the evaluation of the remedial action alternatives.
- recommend the most cost-effective technically feasible remedial option which has the ability to reduce impacts on human health, welfare and the environment to an acceptable level.
- prepare a conceptual design of the recommended remedial action alternative.

TASK 1 - DESCRIPTION OF CURRENT SITUATION

O'Brien & Gere has obtained available background information pertinent to the sites. The data gathered during any previous investigations or inspections and other relevant data were used in developing the RI work plans. A partial list of sources on published and unpublished data available on Crab Orchard Creek watershed and Crab Orchard Lake is included in the Work Plan Supplement (December 1985).

The sub-tasks include site background, nature and extent of the problem at the sites under investigation and a history of response actions.

TASK 2 - REMEDIAL INVESTIGATION SUPPORT

Prior to initiating the Phase I field investigations, the following preliminary work was completed.

A. Site Visit

Initial site visits were conducted to become familiar with site topography, access routes, and proximity of receptors to possible contamination, and to collect data to support the Site Health and Safety Plan. Site surveys were conducted to identify and stake boundaries of known contaminated areas, monitoring wells, and soil borings, and to identify sediment sample locations for Phase I sampling and analysis. The visit was used to verify the site information developed in Task 1. The Site Health and Safety Plan was amended as a result of this visit.

B. Site Maps

As part of the Remedial Investigation Report, O'Brien & Gere will prepare site maps showing all wetlands, water features, drainage patterns, tanks, buildings, utilities, paved areas, easements, right-of-ways, and other features. The site maps and all topographic surveys will be of sufficient detail and accuracy to locate and report all existing and future work performed at the sites. Areas of investigation will be mapped using existing topographic maps or aerial photos. After the analytical data have been reviewed and where necessary for remedial efforts, the topographic maps will be prepared with 1-foot contours referenced to the National Geodetic Vertical Datum with a scale of 1 inch to 50 feet. The maps will extend 200 feet beyond site boundaries and include all drainages to Crab Orchard Lake.

Boundary lines encompassing contaminated areas will be identified. The boundary lines for the landfill study sites will be identified using results from magnetometer and electromagnetic measurements. The boundary conditions will be set so that subsequent investigations will cover the contaminated media in sufficient detail to support the feasibility study. The boundary conditions may also be used to identify boundaries for site access control and site security. If necessary, a fence or other security measures may be installed as an initial remedial measure.

C. Dispose of On-Site Generated Waste

All wastes generated by on-site activities will be labelled, drummed and stored within controlled-access areas. Wastes which will be drummed include: all drill cuttings, all purged groundwater from well development, decontamination wash water and disposable protective clothing. This practice was followed during Phase I investigations. These materials, if contaminated, will be properly disposed of during cleanup actions as identified by the feasibility study.

TASK 3 - SITE INVESTIGATIONS

The remedial investigations include components necessary to characterize the site and its actual or potential hazard to public health and the environment. The site investigations will generate data of adequate technical content to support detailed evaluations of alternatives during the feasibility studies.

The sites listed in Table 1 fall under five categories.

1. Landfills
2. Surficial Contaminant Sites
3. Streams
4. Ponds
5. Lake

The sub-tasks under site investigations include:

- A. Geophysical Surveys
- B. Hydrogeologic Investigations
- C. Groundwater Sampling and Analysis
- D. Soil Investigation

E. Surface Water and Sediment Sampling and Analysis

F. Fish Sampling and Analysis

The site investigations include two phases. Phase I, which was completed in November 1985, included geophysical surveys, hydrogeologic investigations, installation of groundwater monitoring wells, and a screening of each site to analyze composited samples for a broad array of potential contaminants as listed in Table 2A. Selected samples were confirmed by a full analysis for priority pollutants.

Phase II, for which this QAPP has been developed, consists of the additional sampling and analysis to fill in data gaps identified in Phase I and further assess the extent of contamination at sites where materials of concern are found. Analytical parameters included for Phase II Site Investigations are listed in Table 2b *with reference to Table 2C,*

A. Geophysical Surveys

Geophysical investigations were conducted in Phase I to determine the extent of soil and groundwater contamination, if any, in the vicinity of several specified study sites. In particular, the geophysical investigations were conducted at areas of suspected landfill activities, and consisted of magnetometer and electromagnetic induction (EM) surveys.

B. Hydrogeologic Investigations

The results from hydrogeologic investigation will be used to determine the present and potential extent of groundwater contamination, if any, and to evaluate the suitability of the site for on-site waste containment. Efforts began with a

*The plan is
no longer to
meet the goals.*

survey of previous hydrogeologic studies and other existing data (completed as part of Task 1 a and c). The survey along with additional work in this investigation will address the degree of hazard, the mobility of chemicals considered, the soil attenuation capacity and mechanisms, discharge/recharge areas, regional flow direction and quality, and effects of any pumping alternative. Sampling programs for this Remedial Investigation has been developed to determine the horizontal and to vertical distribution of chemicals considered and predict the long-term disposition of such chemicals.

C. Sampling and Analyses of Groundwater

*Not to
include hydrogeology
section additional
work needed before
sample*

Nine groundwater monitoring wells were installed during the Phase I field effort. Additional monitoring wells will be installed during Phase II. All the monitoring wells will be sampled and the water analyzed for contaminants of concern.

Then, based on the geophysical results (Task 3a) and results of contaminant analyses, the extent and scope of any additional hydrogeologic investigation will be determined.

D. Soil Investigation

The two phased investigation program was developed to identify the location and extent of surface and subsurface soil, and sediment contamination. This process overlaps with certain aspects of the hydrogeologic study, e.g.,

characteristics of soil strata are relevant to both the transport of contaminants by groundwater and to the location of contaminants in the soil. Several soil samples and soil borings were collected for analysis from various sampling sites around the refuge during Phase I. Additional samples are scheduled to be collected in Phase II.

E. Surface Water and Sediment Investigation

O'Brien & Gere has developed and conducted a Phase I program to determine the overall extent of any water and sediment contamination on selected refuge lakes, marshes, ponds and streams. The initial process will overlap with the investigations scheduled in Phase II.

F. Fish and Wildlife Investigations

Selected species of fish have been collected, during Phase I, from Crab Orchard Lake by the FWS.

Table 7A lists the species and number of fish per site. Fish samples will be filleted (see Attachment 3) and analyzed for residual levels of contaminants previously identified in landfills and other contaminated areas on the refuge. Skin-on fillets will be used for carp and bass and skin-off fillets for catfish and bullhead. Additionally, percent lipids will be determined on the fish portions selected for analyses.

TASK 4 - PRELIMINARY REMEDIAL TECHNOLOGIES

A. Post-Investigation Evaluation

Either during or following the site investigations, O'Brien & Gere will assess the investigation results and recommend preliminary remedial technologies best suited to specific contaminant problems for each site. They will provide the basis for developing detailed alternatives needed for the completion of the feasibility studies. The data generated during the remedial investigations will generally be limited to accomplish the following:

1. Recommend types of remedial technologies appropriate to physical and site contaminant conditions.
2. Recommending whether or not to remove some or all of the waste for off-site treatment, storage, or disposal.
3. Determine the compatibility of groups of wastes with other wastes and with materials considered as part of potential remedial action. Recommend alternatives for treatment, storage, or disposal for each category of compatible waste.

TASK 5 - SITE INVESTIGATIONS ANALYSIS

The results of Tasks 1 through 4 will be used to prepare a thorough analysis and summary of all site investigations. The objective of this task is to ensure that the investigation data are sufficient in quality and quantity to support the feasibility studies.

The results and data from all site investigations will be organized and presented logically. The geographic groupings listed on Table 1

will form the basic structure for all of the assessments. This will permit the assessment of transport modes and impact to receptors.

A. Data Analysis and Endangerment Assessment

The site investigation data will be analyzed to develop a summary of the type and extent of contamination at the sites. The summary will describe the quantities and concentrations of specific chemicals at each site and ambient levels surrounding the sites. Ambient samples will be collected from control sites.

Data collected during the RI phase will also be evaluated to determine if environmental conditions or materials at the site present potential hazards to human health or welfare, or to the environment. Existing standards will be reviewed to help formulate conclusions and recommendations regarding the hazard potential of the site. If additional hazards are identified, the risks associated with each hazard will be summarized.

This analysis will discuss the degree to which either source control or off-site measures are required to significantly eliminate the threat, if any, to public health or the environment. If the results of the investigation indicate that no threat or potential threat exists, a recommendation of no remedial response will be made.

A technical memorandum will be prepared by the Respondents summarizing the hazard evaluation process and presenting the results of the hazard assessment.

TASK 6 - FINAL REPORT

A final RI report will be prepared to consolidate and summarize the data collected during the RI. The report will include a discussion of the data acquired during the RI and the hazard identification and risk potential of the contaminants detected. Ten copies of the remedial investigation report will be submitted to the FWS. The report will be structured to enable the reader to cross-reference with ease.

TASK 7 - COMMUNITY RELATIONS

The Community Relations program is included as Task 7; however, the dissemination of information to the public will be coordinated by the FWS throughout the duration of the study. O'Brien & Gere will provide personnel, at the Service's discretion, to support the programs as community relations must be integrated closely for all remedial response activities.

The objectives of this effort are (1) to keep the community informed as to the study progress, (2) to achieve community understanding of the actions taken, and (3) to obtain community input, and support prior to selection of the remedial alternative(s).

TASK 8 - ADDITIONAL REQUIREMENTS

A. Reporting Requirements

O'Brien & Gere will prepare monthly reports to describe the technical and financial progress of the project. These reports will discuss the following items:

1. Identification of sites on which activity took place and the nature of those activities.
2. Status of work at the site and programs to date.
3. Percentage of completion.
4. Difficulties encountered during the reporting periods.
5. Actions being taken to rectify problems.
6. Activities planned for the next month.
7. Changes in personnel
8. A comparison of target and actual completion dates for each element of activity including project completion and an explanation of any schedule deviations in the work plan.
9. Progress Reports on Items 1 through 8 will be submitted to FWS, who shall in turn relay them to USEPA and IEPA.
10. A Work Plan that includes a detailed technical approach and schedules will be submitted for the proposed feasibility study.

B. Site Health and Safety Plan

Prior to conducting any field activities O'Brien & Gere will provide any necessary modifications to the Site Health and Safety Plan as presented in Appendix C of the Work Plan dated June 1985. The plan is consistent with:

Section 111(c)(6) of CERCLA.

EPA Order 1440.3 - Respirator Protection

EPA Order 1440.2 - Health and safety requirements for
employees engaged in field
activities.

EPA Occupational Health and Safety Manual.

Other EPA guidance as provided.

State Safety and health statutes.

Site conditions.

EPA Interim Standard Operating Safety Guide (September
1982) and applicable OSHA standards.

C. Quality Assurance/Quality Control (QA/QC)

O'Brien & Gere has prepared a Quality Assurance Project Plan (QAPP) for the sampling, analysis, and data handling aspects of the remedial investigation which is presented in Appendix A of the Work Plan dated June 1985. The QAPP plan is consistent with U.S. Fish and Wildlife Service, State and Federal EPA requirements. The plan addresses the following points:

1. QA Objectives for Measurement Data, in terms of precision, accuracy, completeness, representativeness and comparability.
2. Sampling Procedures.
3. Sample Custody.
4. Field Equipment, Calibration Procedures, References and Frequency.
5. Internal QC Checks and Frequency.

6. QA Performance Audits, System Audits, and Frequency.
7. QA Reports to Management.
8. Preventative Maintenance Procedures and Schedule.
9. Specific Procedures to be used to routinely assess data precision, representativeness, comparability, accuracy, and completeness of specific measurement parameters involved. This section will be required for all QA project plans.
10. Corrective Action.

D. Site Sampling Plan

Site specific sampling plans for Phases I and II of site investigations have been developed for this Remedial Investigation, and are summarized in Section 1.05 of this QAPP. The sampling plan covers the sampling efforts described in the Remedial Investigation work plan and addresses the following topics:

- o Sample types and tentative locations
- o Sample equipment and procedures
- o Sample handling, custody procedures, and preservation
- o Sample documentation
- o Sample shipping
- o Analytical arrangements (scheduling)
- o Analytical procedures
- o QA/QC review procedures of data
- o Analytical review of data

- Disposal of unused samples

1.05 Sampling and Analysis

Phase I sampling and analysis details are set forth in Appendix B of the Site Sampling Plan dated 6/85. Additional details are included in the Work Plan Supplement dated 12/85. *have been completed and*
The Phase I sampling results and the proposed
The Phase II sampling program is presented in detail in the Work Plan Supplement, Phase II Site Operations Plan dated *9/86* *update* ~~4/86~~.

Sampling activities under various Remedial Investigation Tasks are shown in Table 4. A listing of individual samples scheduled and rationale for Phases I and II sampling and analysis are included in the Work Plan Supplement - Phase II Site Operations Plan, September 1986. For Phase I, a summary of the analysis sets and sampling and analysis by sites, analysis sets and sample types are presented in Tables 5 and 6. For Phase II, detailed sampling and analysis by site, parameters and sample types is presented in Table 7.

1.06 Project Schedule

The proposed project schedule is illustrated in Figure 2. This schedule was developed for planning purposes. Several tasks identified in the Work Plan emphasize uncertainties or contingent items which may be defined at a later date depending on the results of analytical data or engineering assessments. Therefore, schedule modifications may be necessary as these tasks are encountered.

Fig 2 is a generic project schedule. Replace it with a time table identifying tasks completed and task projected to be completed.

I think Dick intended to put the responsibility
on interpretation review rather than review of the
quality of the data or measurements. Identify exactly
the type of review Dick intends to provide.

Section No: 2
Revision No: 2
Date: Sept. 2, 1986
Page 1 of 4

SECTION 2 - PROJECT ORGANIZATION AND RESPONSIBILITY

2.01 Functional Activities

Table 8 lists the functional activities of this project and the firms responsible for the particular activity.

2.02 Project Organization

Table 9 lists the primary contacts for the project. Project technical personnel and quality assurance personnel are indicated in the project organization chart (Figures 3 and 4 respectively). Primary responsibility for project quality review rests in the NWR Resource Contaminants Assessment Coordinator. Independent quality assurance review is provided by the Columbia National Fisheries QA/QC representatives, the refuge manager, and the USEPA On-Scene Coordinator.

Additionally, the USEPA will serve in a review capacity on issues that relate to human health, while the FWS functions in a equal capacity on issues that impact on wildlife. The USEPA will also supply performance evaluation samples and conduct performance and system audits.

2.03 Project Manager

The Project Manager will have primary responsibility for overseeing all facets of the project on a day-to-day basis. Specifically, his duties will include:

- Project scheduling
- Budget control
- Subcontractor performance review

Again I don't think the manager nor I will be
a formal quality assurance review of the measurements. Our role is
more interpretive review and oversight.

- Review of interim reports
- Responsible for project coordination and communication
- Project deliverables
- Responsible for establishing a project specific record keeping system
- Project close-out

To accomplish the wide range of analysis, it is intended to utilize the services of three laboratories. The following list identifies the laboratories and analysis performed.

OBG Laboratories, Inc. - Syracuse, New York

PCB's - all samples scheduled

Inorganics - all samples scheduled

Metals - (Flame) - all samples scheduled

Mercury - (cold vapor) - all samples scheduled

Environmental Testing and Certification (ETC) - Edison, New York

CLP Organics - all samples scheduled

PCDD's and PCDF's - all samples scheduled ~~— not scheduled~~

Ray F. Weston - Westchester, PA

Explosive - all samples scheduled

Rocky Mountain Analytical Laboratory - Wilson Laboratories

Metals (furnace) - all samples scheduled

143 Project Manager
2.04 Quality Assurance Officer

Inconsistent

The Quality Assurance (QA) Manager is responsible for the monitoring and supervision of the QA/QC program. The QA Officer reports directly to the Project Manager and his responsibilities include:

- Insure field personnel are both familiar with and adhering to proper sampling procedures, field measurements sample identification and chain-of-custody procedures.
- Contact the laboratory to insure that samples received by them have been properly identified and packaged.
- Monitor and audit the performance of the QA procedures.
- Conduct field and office audits.
- Insure that USEPA performance audit samples are incorporated into the system as deemed appropriate.
- Maintain a record of performance and system audits and inform the Project Manager of any problems encountered in the analytical procedures.
- The QA Officer in conjunction with the Project and Laboratory Managers will formulate recommendations on corrective action procedure to correct any deficiency in the analytical protocol, data, or sampling.

2.05 Assistant Project Managers

The management team for this project will draw upon the technical expertise and experience of a number of different individuals. The project team will consist of multidisciplined personnel with expertise in Aerial Photograph interpretation, hydrogeology, geophysical surveys, chemical characterization, soil science, wet chemistry and toxicology. The firms toxicologist will be responsible for the development of both the Safety Plan and the Risk Assessment.

2.06 Manager of Analytical Services

The Laboratory Manager is responsible for the overall administration of the analytical operations at O'Brien & Gere. The section group leaders handle the day to day operations and scheduling and report to the manager.

The Laboratory Quality Assurance Manager is responsible for the implementation, monitoring and supervision of the QA/QC program. He assures that the program is conducted in strict adherence to procedures and requirements outlined for this program. He reports to the Laboratory Manager and interacts daily with other group leaders and laboratory staff. His duties include:

- Insuring laboratory custody procedures are followed.
- Monitors daily precision and accuracy records.
- Maintains copies of all procedures routinely used.
- Implements correction measures if results are "out of control"
- Reschedules analysis based upon unacceptable accuracy or precision data.

Who is responsible for:
~~conducting performance & system audits~~
supplying PE samples - USEPA
data validation - O&G initial
data assessment - validation by USEPA & FED

U.S. EPA, CRL will assess all Phase II data.

SECTION 3 - QUALITY ASSURANCE OBJECTIVES

3.01 Overall Objectives

The general quality assurance objective for analyzed measurement data is to ensure that environmental monitoring data of known and acceptable quality are provided.

For this project, the specific objectives for measurement data in terms of precision, accuracy and compatibility are the same as the objectives established for the Statement of Work for the U.S. EPA Contract Laboratory Program (CLP), viz.: The purpose of the QA/QC program....is the definition of procedures for the evaluation and documentation of subsampling, analytical methodologies, and the reduction and reporting of data. The objectives are to provide a uniform basis for subsampling, sample handling, instrument condition, methods control, performance evaluation, and analytical data generation and reporting." This QAPP for sampling, analysis and data handling is consistent with the requirement set forth by the U.S. Fish and Wildlife Service, as well as all State and Federal EPA requirements.

3.02 Field QC Objectives and Procedures

Field functions such as; magnetometer and electromagnetic terrain conductivity services performed during Phase I are activities which do not include sample collection, but involve measurements where quality assurance concerns are appropriate. The primary objective in activities such as these is to obtain reproducible measurements consistent with their intended use.

Problems:

1. Different procedures for PCB's.
2. Lower detection limits required for PCB's & nitrosamines in drinking water. This needs to be defined & outlined how to document.

- 3
- Sampling procedures to be used at the site
 - Tests to be completed at each sampling location
 - Sampling equipment required at the site
 - Sample containers required at the site
 - Preservation methods to be used at the site for various types of samples
 - Reagents, etc., required at the site for sample preservation
 - Shipping containers required at the site
 - Chain-of-custody procedures to be used at the site
 - Shipping methods and destinations, marking instructions, special labels, etc.

3.03 Field QC Audits

Blanks and duplicate samples will be collected as part of our QA/QC program. Blanks are employed to ensure that neither glassware nor procedural contamination has occurred. Additionally, they are utilized to evaluate ambient site conditions which may cause sample contamination. If positive interferences occur, the Quality Assurance Officer will recommend to the Project Manager that sample collecting and handling procedures be technically reviewed to eliminate such sample contamination.

Duplicate samples are treated throughout as two unique samples. The results of duplicate analyses provide information on the overall precision of both the sampling and analytical programs.

The number of duplicate and spikes samples for Phase I and II are summarized in Table 7.

no it isn't!

3.04 Accuracy, Sensitivity and Precision of Analysis

Samples collected during Phase II will be analyzed using procedures presented in Table 10. Additionally, Table 10 contains, method detection limits, audit, frequency and control limits.

This does not include the special analytes or objectives for the low level PCB's and nitroamines in the drinking water samples.

It does not include the special extraction procedures for PCB's used by A'Brien & Gere.

SECTION 4 - SAMPLING PROCEDURES

4.01 Objective

Crab Orchard National Wildlife Refuge is the Sept. 1986 Site Under Review

The objective of this Sites Sampling Plan (SSP) is to document the ~~sampling locations~~, procedures and practices that will be used in the Remedial Investigation sampling program to be conducted at Crab Orchard National Wildlife.

It has been determined that the sampling and analysis program at Crab Orchard National Wildlife Refuge will be accomplished in two phases.

has been completed and is for ing whether a problem exists as necessary

Phase I ~~will be the basis used to determine if a potential problem (s) exists on a specific site and to characterize the range of chemical compounds which contribute to the problem.~~ Phase II will be employed to define the extent of contamination (both vertically and laterally) of any site identified during Phase I as a area of concern. The information obtained during Phase II will be used in evaluating the remedial options.

In general, the analytical effort associated with Phase II will be less than that of Phase I, because the results of the initial effort will assist in diminishing the total number of sites and reducing both organic and inorganic constituents of concern.

4.02 Types of Samples

Various matrices will be sampled and analyzed as part of the Remedial Investigation. These include the following:

1. Waters: including ground waters, surface streams, raw and finished water supplies, pond waters and waters from Crab Orchard Lake.
2. Sediments: from streams, ponds and Crab Orchard Lake.
3. Soils: including soils potentially affected by surface spillage and fill material from sites of past disposal activity.
4. Air: as part of the site safety program.
5. Biota: including fish, turtles and crayfish.

For the most part, all samples will be obtained as single grab samples. No time-composited samples are contemplated. However, at many sites, areal soil composites will be prepared. Areal composites are used as a screening device to allow initial assessments of broad areas for a range of contaminants. Compositing procedures are discussed below.

Eliminate: This is not being done during Phase II,

4.03 Compositing Procedures

~~Areal composites of water samples (along stretches of streams, surfaces of ponds or~~ Depth composites in Crab Orchard Lake) will be prepared by combining equal volumes of grab samples at each location.

The nine water and sediment locations identified in the Work Plan, June 1985, and one control site in the western end of Crab Orchard lake will be sampled during Phase II, to determine the extent of water and/or sediment contamination.

A composite water sample from each of the 10 Lake locations will be obtained as follows: discrete samples from the surface, mid-depth and approximately six inches from the bottom will be taken using a

*Eliminate
is not being
done during
Phase II*

*more than
9. sec
6/25 W.P.*

*eliminate
delete*

This is confusing because, I don't know which site you are referring to. These procedures should be explained on a site specific bases.

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Kemmerer bottle. Equal aliquots from each of the three depths at each site will be composited and preserved according to the procedures listed in Attachment 2 of the Work Plan dated June 1985. *incorporate this table.*

The question of thermocline most often applies to deep bodies of water. Crab Orchard lake has a mean depth of 3 meters and a maximum depth of 10 meters in the western portion of the lake. The eastern portion of the lake is shallow, hence, is not expected to have a significant change in temperature with depth and therefore the above compositing method will accomplish the Phase II objective, to define the extent of contamination both laterally and vertically.

Individual grab samples for volatile organic analyses will be retained and labelled in individual headspace-free vials for compositing by the laboratory.

Areal composites of soil/sediment samples will be obtained by combining equal volumes of grab samples from predetermined locations.

Soil/sediment grabs will be obtained using standard geological tools (shovels, scoops, etc.) to a depth of 3 inches. The discrete samples will be placed into a (disposable) aluminum pan and homogenized by hand, using a large stainless steel spoon. The composited sample is then placed into appropriate (pre-labeled) sample containers and refrigerated (0-4°C).

4.04 General Sampling Locations and Numbers

Sample Locations

Phase I

Sampling locations were determined in the field during a site reconnaissance visit on March 26-28, 1985. They are presented in

We're mainly concerned with Phase II sample locations. Reference the 9/86 WP Supplement to identify.

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the Site Sampling Plan (Dec. 1985). A log book listing the various samples to be collected will be prepared for use on-site. The log book will also contain the type of sample and analytical matrix for each of the samples to be collected. Pre-printed peel-off labels will be included in the log book for tagging the various containers to be used for sample collection. The sample team leader will be responsible for determining the exact sampling location and recording the location in the field sampling notebook. The location will be described in the log book with a sketch that includes distances from numbered field reconnaissance stakes and other landmarks. The rationale of selecting a sampling location will also be included. All sampling locations will be photographed.

Sample Numbering System

A sample numbering system will be used to identify each sample taken during the remedial investigation sampling program. This numbering system will provide a tracking procedure to allow retrieval of information regarding a particular sample and to assure that each sample is uniquely numbered. A listing of the sample identification numbers will be maintained by the sample team leader.

4.05 Sampling Equipment and Sampling Procedures

Soil Sampling

Equipment and supplies for the Phase II sampling activities are enumerated in Attachment 4.

As much as possible, the sampling equipment that comes in to contact with the sample should be stainless steel or Teflon.

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Additionally, all sampling equipment, except disposables, such as aluminum pans, will be decontaminated between sampling sites.

As much as possible of the sampling equipment should be pre cleaned and disposable.

The General Decontamination procedures for sampling equipment are given on pages 9 then 11 of this section.

Soil samples will be collected from identified spots around the Refuge and during the installation of additional groundwater monitoring wells. Samples will be collected in general accordance with the split spoon sampling procedure (ASTM D1586-67), using 2-inch OD split spoon samplers.

Groundwater Studies and Sampling

Reference method of measurement and interpretation

To perform a "slug" test or in-site hydraulic conductivity test, a potential hydraulic difference must be created between the well being monitored and the surrounding aquifer.

Use stainless steel.

This will be accomplished by rapidly inserting a solid piece of one-inch (1") diameter ~~PVC~~ into the water column in the well, thereby displacing the water column upward in the well and creating a potential for flow from the well to the surrounding aquifer. The rate of decline of the water level in the well will be monitored as it again comes into equilibrium with the aquifer.

Subsequent to the well water level approaching the pre-induced hydraulic head static level, the displacing rod will be removed. This will result in a water level in the well that is lower than the surrounding aquifer and therefore will create a potential

for flow from the aquifer into the well. This recovery will also be monitored until the static level is approached.

Groundwater levels during the tests will be monitored using an Enviro-Labs Data Logging System which employs a conventional analog signal generating pressure transducer that directly measures feet of hydraulic head to the one-hundredth (0.01) of a foot.

Aquifer slug recovery tests will be conducted in all ~~additional~~ monitoring wells to obtain in situ estimates of hydraulic conductivity. A minimum of two test runs should be made at each test well.

schedule 316

main casing → All monitoring wells will be constructed of *stainless steel* well screen and TIMCO or equivalent P.V.C. riser casing that will extend from the screened interval to 2'-3' above existing grade.

only for well /
rest of casing
will be PVC
Q-Rock Other materials utilized for completion will be washed silica sand (Q-Rock Number 4 or approved equivalent) bentonite grout, Portland Cement and a protective steel locking well casing and cap with locks.

Wells will be installed using a hollow stem auger. → The monitoring well installation method for 2" wells installed within unconsolidated sediments shall be to place the screen and casing assembly into the auger string once the screen interval has been selected. At that time a washed silica sand pack will be placed if required to prevent screen plugging. If a sand pack is not warranted, the auger string will be pulled back to allow the native aquifer material to collapse 2-3' above the top of the screen. Bentonite grout will then be added to the annulus

between the casing and the insider auger wall via a tremie pipe to insure proper sealing. Grout will continue to be added during the extraction of the augers until the entire aquifer thickness has been sufficiently sealed off from horizontal and/or vertical flow above the screened interval. During placement of sand and bentonite frequent measurements will be made to check the height of the sand pack and thickness of bentonite-layers by a weighted drop tape measure.

Pre lean casing with detergent and rinse. ➤ A vented protective steel casing shall be located over the PVC standpipe extending two (2) feet below grade and 2-3' above grade secured by a Portland Cement seal. The cement seal shall extend laterally at least one foot (1') in all directions from the protective casing and shall slope gently away to drain water away from the well. A vented steel cap will be fitted on the protective casing and a steel hasp shall be welded on one side of each steel casing so the cap may be secured with a steel lock.

The supervising geologist shall specify the monitoring well design to the Drilling Contractor before installation.

Properly decontaminated equipment will be used in sampling all groundwater monitoring wells. See General Decontamination Procedures Section 4 of this QAPP. Before samples are taken, each well will be purged until there is a constant conductivity, (usually about 5 to 10 well volumes). After the well has recovered, samples for inorganic and organic (excluding volatiles) analysis can be collected. All wells will be sampled using hand bailers constructed of stainless steel or Teflon. Ground water

A separate bailer for each well is desirable.

samples will be split in the field. A aliquot will be filtered through a 0.45 micron membrane filter and preserved for dissolved metal analyses. A second portion will be preserved for total metals. Additionally, a sample will be taken for total suspended solids. Samples to be analyzed for organics will not be filtered.

Waste Sampling

*Also Site 28 Water Tower
Landfill.*

The Area 9 Landfill is the only site of the Refuge where waste materials are being sampled. All other sites represent sampling of matrices potentially affected by dispensed contaminants. There are special safety concerns posed by the sampling of waste materials at Area 9 because of the possible presence of explosives residues or even undetonated cartridges. Similar concerns exist at other sampling sites, but sampling elsewhere is limited to within 1 foot from the surface. Soil borings at Area 9 will employ split spoon sampling procedures. Drilling personnel will be required to be removed at least 100 ft. from the drill rig during advancement of the augers. This is further discussed in the SHSP.

Field Blanks

Field Blanks for sediment and soil samples will consist of analytical grade diatomaceous earth. For water samples, ultrapure distilled/deionized water will be used. The field blank sample will be placed into the appropriate ^{decontaminated} sampling equipment, removed from the equipment, and then placed into sampling containers.

Duplicate Samples

Duplicate samples are defined as two distinct samples taken from the same location at similar times using identical sampling equipment that has been decontaminated in a similar manner. However, duplicate samples of soil cores will consist of a given core homogenized, divided equally and submitted for analysis as two distinct samples.

Split Samples

A number of samples will be split with a representative of the FWS for analysis. Split samples are defined as one distinct sample that is divided equally and sent to two different laboratories for analysis. Soils will be field homogenized in a clean aluminum pan prior to splitting. Water sample splits will be duplicates.

4.06 General Decontamination Procedures

Decontamination of personal gear (boots, gloves, and waders), sample jars and sampling equipment will be as follows (see also attached materials to the SHSP):

1. Wash personal gear or sample containers in a bucket or tub filled between 50 and 75 percent with a trisodium phosphate (TSP) solution (2 lbs of TSP per 10 gallons of clean water). Completely brush the entire exterior surface of the article undergoing decontamination. If PCB's are expected to be present, add 4 lbs of sodium bicarbonate per 10 gallons of water to the washing solution.

2. Rinse personal gear or sample containers in a bucket or tub filled between 50 and 75 percent with clean water. Completely brush the entire exterior surface of the article undergoing decontamination.
3. Dispose of all wash and rinse water in a properly marked and sealed container. All such containers of wastewater will be stored in a secure area on-site and properly disposed of during the remedial action phase.

4.07 Sampling Equipment

Sampling equipment should be pre-cleaned before use to avoid contamination and then cleaned into samples.

1. Wash sampling equipment in a bucket or tub filled between 50 and 75 percent with a TSP solution (2 lbs of TSP per 10 gallons of clean water). Completely brush the entire exterior surface of the article undergoing decontamination. Wash interior wetted surfaces as required. If PCB's are expected to be present, add 4 lbs of sodium bicarbonate to the washing solution. Drilling equipment, augers and split spoon samplers can be decontaminated by steam cleaning using clean water.

2. Rinse only heavily contaminated sampling equipment in a bucket or tub filled between 50 and 75 percent with a ~~20 percent solution of acetone and water~~ ^{methanol}. Completely brush the entire exterior surface of the article undergoing decontamination. Rinse interior wetted surfaces as required. If PCB's are present, the first rinse should be carried out with a hexane solution.

Why only heavily contaminated sampling equipment?

3. Following step 2 above, rinse all sampling equipment in a bucket or tub filled between 50 and 75 percent with distilled water.

Completely brush the entire exterior surface of the article undergoing decontamination. Rinse interior wetted surfaces as required.

4. Collect all wash and rinse water in a properly marked and sealed container. Wash and rinse water will be analyzed relative to its hazardous waste characteristics and disposed of in accordance with all applicable state and federal regulations. Drilling soils and water as well as discarded protective clothing will be treated similarly.

4.08 Documentation

Site Location Procedure

Following sampling location identification, a wood stake (approximately 2" X 2" X 24") will be driven into the ground, allowing approximately 8 to 10 inches of the stake to remain visible above ground. The top portion of the stake will be painted orange and labeled for identification. The label will contain sample number and sample type. The location of each stake will be recorded. Sample locations will eventually be surveyed and tied into the site grid system.

4.09 Photographs

Photographs (35mm, color slides) will be taken to illustrate sampling locations. Photographs will show the surrounding area and reference objects which help to locate sampling sites. The picture number and roll number (if more than one roll of film is used) will be logged in the field notebook to identify which sampling site is depicted

in the photograph. The film roll number will be identified by taking a photograph of an informational sign on the first frame of the roll. This sign would have the job and film roll number written on it to identify the pictures contained on the roll.

4.10 Field Notebooks

Field notebooks will provide the means of recording data on collecting activities performed at a site. As such, entries will be described in as much detail as possible so that anyone going to the site could reconstruct a particular situation without reliance on memory.

Field notebooks will be bound. Notebooks will be assigned to field personnel, but will be stored in the document control center when not in use. Each notebook will be identified by the project-specific document number.

The cover of each notebook will contain:

Person or Organization to whom the book is assigned.

Book Number

Project Name

Start Date

End Date

Entries into the notebook will contain a variety of information. At the beginning of each entry, the date, start time, weather, all field personnel present, level of personal protection being used onsite, and the signature of the person making the entry will be entered. The names of visitors to the site, all field sampling team personnel and the purpose of their visit will be recorded in the field notebook.

All measurements made and samples collected will be recorded. All entries will be made in ink with no erasures allowed. If an incorrect entry is made, it will be crossed out with a single strike mark. Whenever a sample is collected or a measurement is made, a detailed description of the location of the station, which includes compass and distance measurements, shall be recorded. The film roll number and number of photographs taken of the station will also be noted. All equipment used to make measurements will be identified, along with the date of calibration.

Samples will be collected following the procedures documented in this plan. The equipment used to collect samples will be noted, along with the time of sampling, sample description, depth at which the sample was collected, volume and number of containers. In addition, the cooler number into which the sample is placed in the field will be recorded. Sample numbers will be assigned prior to going onsite. Duplicates, which will receive an entirely separate sample number, will be noted under sample description. Significant field notebook entries (samples collected, significant observations) shall be countersigned by another member of the project team.

4.11 Control of Contaminated Sampling Materials

Disposable sampling and safety equipment and excess samples may be generated during sampling operations. These materials will be placed into drums (separate drums for solids, decontamination liquids, debris, and disposable equipment).

Decontamination liquids should also be separated based on those containing solvents (acetone, hexane, etc.) and those containing only detergents (TSP, etc.). The drums will be sealed, labelled and properly stored in a secure area for proper, legal disposal during the remedial action phase. Bailed well water and contaminated drilling spoils will be drummed for proper storage in a secure area.

Sample Control

Serialized sample tags will be used to label each sample for analysis. Chain-of-custody records will be completed for all samples according to EPA requirements and procedures set forth in NEIC Policies and Procedures EPA-330-19-78-001R (Revised 1986). Custody seals will be placed on all shipping coolers containing samples.

4.12 Sample Containers and Sample Preservation

Required sample containers, filling instructions and preservation procedures are listed below. The collected samples will be kept out of direct sunlight and, after decontamination and labeling, will be placed in coolers for shipment to the analytical laboratory.

Sample containers will be supplied by the O'Brien & Gere's laboratory. In order to insure both sufficient quantity and proper container cleanliness the contract laboratory will order these supplies from I Chem Research, Inc. located in Hayward California. When ordering the containers the contract laboratory will specify pre-cleaned jars with teflon liners.

The types of containers are as follows:

A - Water

- °125 ml screwcap glass with teflon liner
- °100 ml polyethylene bottle with screw cap
- °40 ml VOA vials with teflon septum
- °500 ml polyethylene bottles with screw caps
- °quart glass jars with teflon lined cap
- °gallon glass jars with teflon lined cap

B - Soil/Sediment

- °40 ml VOA vials with teflon septum
- °30 ml crimp vials
- °60 ml glass jars with teflon lined cap
- °Wide mouth pint glass with teflon lined cap
- °1/2 pint glass with teflon lined cap

*For which
parameters?*
↓

In order to insure container cleanliness randomly selected containers will be filled with distilled deionized water and sent to the laboratory for analyses. The analyses requested for this blank sample will be equivalent to that for which the sample to be held by that container would normally be analyzed for.

RECOMMENDATION FOR SAMPLING AND PRESERVATION
OF SAMPLES ACCORDING TO MEASUREMENT(1)

<u>Measurement</u>	<u>Container</u> ⁽¹⁾	<u>Preservative</u>	<u>Holding Time</u> ⁽²⁾
<u>Physical Properties</u>			
Color	P,G	Cool, 4°C	24 Hrs.
Conductance	P,G	Cool, 4°C	24 Hrs. (3)
Hardness	P,G	Cool, 4°C HNO ₃ to pH 2	6 Mos. (4)
Odor	G only	Cool, 4°C	24 Hrs.
pH	P,G	Det. on site	6 Hrs.
Residue Filterable	P,G	Cool, 4°C	7 Days
Non-Filterable	P,G	Cool, 4°C	7 Days
Total	P,G	Cool, 4°C	7 Days
Volatile	P,G	Cool, 4°C	7 Days
Settleable Matter	P,G	Non Req.	24 Hrs.
Temperature	P,G	Det. on site	No Holding
<u>Metals</u>			
Dissolved	P,G	Filter on site HNO ₃ to pH 2	6 Mos. (4)
Suspended Total	P,G	Filter on site HNO ₃ to pH 2	6 Mos. 6 Mos. (4)
Mercury Dissolved	P,G	Filter on site HNO ₃ to pH 2	38 Days (Glass) 13 Days (Hard Plastic)
Total	P,G	HNO ₃ to pH 2	38 Days (Glass) (Hard Plastic)

*We aren't doing any of
these analyses*

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RECOMMENDATION FOR SAMPLING AND PRESERVATION
OF SAMPLES ACCORDING TO MEASUREMENT (1)
(Continued)

<u>Measurement</u>	<u>Container</u> ⁽¹⁾	<u>Preservative</u>	<u>Holding Time</u> ⁽²⁾
<u>Inorganics, Non-Metallics</u>			
Nitrogen Ammonia	P,G	Cool, 4°C H ₂ SO ₄ to pH 2	24 Hrs.
Kjeldahl, Total	P,G	Cool, 4°C H ₂ SO ₄ to pH 2	24 Hrs. (5)
Nitrate plus Nitrite	P,G	Cool, 4°C H ₂ SO ₄ to pH 2	24 Hrs. (5)
Nitrate	P,G	Cool, 4°C	24 Hrs.
Nitrite	P,G	Cool, 4°C	48 Hrs.
Dissolved Oxygen Probe	G only	Det. on site	No Holding
Winkler	G only	Fix on site	4-8 Hours
Phosphorus Ortho-phosphate Dissolved	P,G	Filter on site Cool, 4°C	24 Hrs.
Hydrolyzable	P,G	Cool, 4°C H ₂ SO ₄ to pH 2	24 Hrs. (5)
Total	P,G	Cool, 4°C H ₂ SO ₄ to pH 2	24 Hrs. (5)
Total, Dissolved	P,G	Filter on site Cool, 4°C H ₂ SO ₄ to pH 2	24 Hrs. (5)
<u>Organics</u>			
BOD	P,G	Cool, 4°C	24 Hrs.
COD	P,G	H ₂ SO ₄ to pH 2	7 Days (5)
Oil & Grease	G only	Cool, 4°C H ₂ SO ₄ or HCl to pH 2	24 Hrs.
Organic Carbon	P,G	Cool, 4°C H ₂ SO ₄ or HCl to pH 2	24 Hrs.

These do not correspond to the parameter categories you have been using.

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RECOMMENDATION FOR SAMPLING AND PRESERVATION
OF SAMPLES ACCORDING TO MEASUREMENT (1)
(Continued)

<u>Measurement</u>	<u>Container</u> ⁽¹⁾	<u>Preservative</u>	<u>Holding Time</u> ⁽²⁾
Phenolics	G only	Cool, 4°C H ₃ PO ₄ to pH 4 1.0 g CuSO ₄ /l	24 Hrs.
MBAS	P, G	Cool, 4°C	24 Hrs.
Nitrosamines	G, Teflon-lined cap	Cool, 4°C store in dark 0.008% Na ₂ S ₂ O ₃ *	7 days until extraction, 40 days after extraction
PCB's	G, Teflon-lined cap	Cool, 4°C ⁸ pH 5-9	7 days until extraction, 40 days after extraction
Nitroaromatics and Isophorone	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Polynuclear aromatic Hydrocarbons	G, Teflon-lined cap	Cool, 4°C store in dark 0.008% Na ₂ S ₂ O ₃ *	7 days until extraction, 40 days after extraction
Haloethers	G, Teflon-lined cap	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ *	7 days until extraction, 40 days after extraction
Chlorinated Hydrocarbons	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
TCDD	G, Teflon-lined cap	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ *	7 days until extraction, 40 days after extraction
Pesticides	G, Teflon-	Cool, 4°C pH 5-9 ⁸	7 days until extraction, 40 days after extraction

* Isn't the Na₂S₂O₃ only for chlorinated
waters?

RECOMMENDATION FOR SAMPLING AND PRESERVATION
OF SAMPLES ACCORDING TO MEASUREMENT(1)
(Continued)

<u>Measurement</u>	<u>Container</u> ⁽¹⁾	<u>Preservative</u>	<u>Holding Time</u> ⁽²⁾
Purgeable Hydrocarbons	G, Teflon-lined septum	Cool, 4°C 0.008% $\text{Na}_2\text{S}_2\text{O}_3$	14 days
Purgeable Aromatics	G, Teflon-lined septum	Cool, 4°C 0.008% $\text{Na}_2\text{S}_2\text{O}_3$ HCl to pH 2	14 days
Acrolein and Acrylonitrile	G, Teflon-lined septum	Cool, 4°C 0.008% $\text{Na}_2\text{S}_2\text{O}_3$ Adjust pH to 4-5	14 days
Phenols	G, Teflon-lined cap	Cool, 4°C 0.008% $\text{Na}_2\text{S}_2\text{O}_3$	7 days until extraction, 40 days after extraction
Benzidines	G, Teflon-lined cap	Cool, 4°C 0.008% $\text{Na}_2\text{S}_2\text{O}_3$	7 days until extraction, 40 days after extraction
Phthalate	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction

1. Plastic (P) or Glass (G). For metals, polyethylene with a polypropylene cap (no liner) is preferred.
2. It should be pointed out that holding times listed above are recommended for properly preserved samples based on currently available data. It is recognized that for some sample types, extension of these times may be possible while for other types, these times may be too long. Where shipping regulations prevent the use of the proper preservation technique or the holding time is exceeded, such as the case of a 24-hour composite, the final reported data for these samples should indicate the specific variance.

RECOMMENDATION FOR SAMPLING AND PRESERVATION
OF SAMPLES ACCORDING TO MEASUREMENT(1)
(Continued)

3. If the sample is stabilized by cooling, it should be warmed to 25°C for reading, or temperature correction made and results reported at 25°C.
4. Where NO₃ cannot be used because of shipping restrictions, the sample may be initially preserved by icing and immediately shipped to the laboratory. Upon receipt in the laboratory, the sample must be acidified to a pH 2 with HNO₃ (normally 3 ml 1:1 HNO₃/liter is sufficient). At the time of analysis, the sample container should be thoroughly rinsed with 1:1 HNO₃ and the washings added to the sample (volume correction may be required).
5. Data obtained from National Enforcement Investigations Center-Denver, Colorado, support a four-week holding time for this parameter in Sewerage Systems. (SIC 4952).

Sample Shipping

Samples will be packed and labelled according to DOT regulations and protocols outlined in the Site Sampling Plan dated June 1985. Samples will be shipped via a 24 hour delivery service to the analytical laboratory so that the samples can be extracted within allowable time limits.

Transfer of Custody and Shipment

1. Samples are accompanied by a Chain-of-Custody Record, Figure 5. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents sample custody transfer from the sampler, often through another person, to the analyst in a mobile laboratory, or at the laboratory.
2. Samples will be packaged properly for shipment and dispatched to the appropriate laboratory for analysis, with a

separate custody record accompanying each shipment (for example, one for each field laboratory, one for samples driven to the laboratory). Shipping containers will be padlocked or sealed for shipment to the laboratory. The method of shipment, courier name(s) and other pertinent information are entered in the bottom of form.

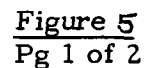
3. Whenever samples are split with a source or government agency, it is noted in the "Remarks" section. The note indicates with whom the samples are being split and is signed by both the sampler and recipient. If either party refuses a split sample, this will be noted and signed by both parties. The person relinquishing the samples to the facility or agency should request the signature of a representative of the appropriate party, acknowledging receipt of the samples. If a representative is unavailable or refuses to sign, this is noted in the "Remarks" space. When appropriate, as in the case where the representative is unavailable, the custody record should contain a statement that the samples were delivered to the designated location at the designated time.
4. All shipments will be accompanied by the Chain-of-Custody Record identifying its contents. The original record will accompany the shipment, and a copy will be retained by the Project Coordinator.
5. If sent by mail, the package will be registered with return receipt requested. If sent by common carrier, a Government Bill of Lading will be used. Air freight shipments are sent

collect. Freight bills, Post Office receipts, and Bills of Lading will be retained as part of the permanent documentation.

Evidence Files

All documents/raw data from the individual laboratories performing specific analysis will be transferred at the end of this RI/FS to the Refuge Manager ^N for safekeeping for a period of 10 years.

*Fish & Wildlife
Service*

[illegible]

RECOMMENDATIONS FOR SAMPLING VOLUME OF SAMPLES ACCORDING TO MEASUREMENT

*These do not cover all the parameters
present that you are using in this project.
The last sample volume to be level, except
nitrosamines in drinking water.*

<u>Measurement</u>	<u>Volume</u>	<u>Container</u>
Metals	1 pt	plastic bottle/cap
Phenols	1 qt	glass bottle/teflon lined cap <u>only</u>
Pesticides	1 qt	glass bottle/teflon lined cap
Herbicides	1 qt	glass bottle/teflon lined cap
Inorganics	1 qt	plastic bottle/cap
Cyanide	1 pt	plastic bottle/cap
Nutrients	1 pt	plastic bottle/cap
Demand	1 pt	plastic bottle/cap
VHO	40 ml	duplicate glass bottle/teflon septum cap
THMS	40 ml	duplicate glass bottle/teflon septum cap
Extractable (base/neutrals/ acid)	1 qt	glass bottle/teflon lined cap
Solids	1 qt	plastic bottle/cap
Oil & Grease	1/2 gal	glass bottle/teflon lined cap <u>only</u>

organics

CONTAINERS

A variety of factors affect the choice of containers and cap material. These include resistance to breakage, size, weight, interference with constituents, cost and availability. There are also various procedures for cleaning and preparing bottles depending upon the analyses to be performed on the sample.

SECTION 5 - SAMPLE CUSTODY

5.01 General

Sample custody procedures for this project will be in strict conformance with the procedures detailed in NEIC Policies and Procedures (EPA-3309-78-001-R). These procedures were established to comply with EPA requirements for sample control. They are documented in Attachment 4 to this QAPP.

All samples collected for analysis will be taken by chemists, physical science technicians, or other qualified personnel designated by O'Brien & Gere with specific instructions from the Project Manager. The FWS will take duplicate samples at a ratio of 1:10 for QA/QC purposes. All samples for residue analysis will be placed in the custody of the analytical chemist responsible for the analysis. The sample information will be recorded on the same report sheets if analyzed immediately. Stored sample (including archive portions) will be catalogued and stored may be audited by the QA Officer. Subsequent to approval of the conceptual design (Task 15), these archived samples will be returned to CONWR for disposal consistent with the remedial action plan.

5.02 Chain of Custody Procedures

The consequences of an uncontrolled hazardous waste site investigation are difficult to predict. There is a possibility that several years after the RI/FS is complete there will be litigation. For that reason, it is imperative that an accurate record be maintained and documented of sample collection, transport, analysis and disposal.

Therefore, chain of custody procedures are instituted and followed throughout the study.

Chain of custody procedures include field custody, laboratory custody, and evidence files. Samples are physical evidence and should be handled according to procedural safeguards. The project coordinator must be prepared to produce documentation that traces the samples from the field to the laboratory and through the analysis. The National Enforcement Investigation Center (NEIC) of the U.S. EPA defines custody of evidence in the following ways:

- In actual physical possession
- In view after being in physical possession
- In a locked repository
- In a secure, restricted area

Chain of custody records begin in the field when sample collection has been completed. See Figure "Chain of Custody Form" for a typical arrangement of the paper samplers use to complete their field logs. On that form, they note meteorological data, equipment employed during collection, evacuation techniques and any calculations, physical characteristics of samples, date, time of day and location, any abnormalities during sampling.

The sampler completes the custody form, packages the samples including the custody form, and seals the package with evidence tape. Shipment may be made by commercial vendors, and their policy is to document the transfer of the package within their organization. Therefore, when the sample arrives at the laboratory, the sample custodian

signs the vendors air bill or bill of lading. The sample custodian's duties and responsibilities upon sample receipt are:

- Document receipt of samples.
- Inspect sample shipping containers for presence or absence of custody seals, locks, evidence tape, container integrity.
- Record condition of shipping and sample containers in logs.
- Sign appropriate forms or documents.
- Verify and record agreement or disagreement of information on sample documents. If there is discrepancy, record the problem and notify the project officer.
- Label sample with laboratory sample number.
- Place samples in ~~storage, including~~ secure storage, ~~if appropriate.~~

The hand-to-hand custody of samples in the laboratory is maintained through preparation and analysis. The analyst is required to log samples into and from secure storage as the analysis proceeds. Samples are returned to secure storage at the close of business. Log sheets incorporate options for multiple entries, because several people handle the samples throughout the analytical scheme. See Figure, "Chain of Custody Form for Analysis."

The laboratory records may also be used as evidence in enforcement proceedings, therefore care must be exercised to properly complete, date and sign items needed to generate data. Copies of the following items are stored:

- Documentation of the preparation and analysis of samples, including copies of the analyst's notebooks.

- Bench sheets, graphs, computer printouts, chromatographic outputs, mass spectral outputs.
- Copies of all QA/QC data.
- Instrument logs showing date, time and analyst.
- Analytical tracking forms which record date, time, and analyst for each step of sample preparation and analysis.

Upon completion of analysis, the project officer or his assignee should commence assimilating all the field and laboratory notes. It is they who generate the evidence file for the project. The package is arranged in chronological order for ease of review. When all the information is gathered, the package is inventoried, numbered and stored for future reference. The document inventory list is illustrated in the following Table:

DOCUMENT CONTROL NUMBER	TYPE	NO. OF PAGES
1111-1	Project file inventory sheets	1
1111-2	Field notes	30
1111-3	Chain-of-custody records	7
1111-4	Shipping manifests	27
1111-5	Sample log-in sheets	40
1111-6	Sample control records	40
1111-7	Sample tickets	500
1111-8	Sample traffic reports	127
1111-9	Analytical traffic reports	127
1111-10	Analytical data summary	10
1111-11	Sample #2	20
1111-12	Sample #3	20
1111-62	Sample #50	20
1111-63	Lab notebook pages	37
1111-64	Bench sheets	50
1111-65	Instrument log pages	13
1111-66	Copies of mass spectral data, graphs, chromatograms	43
1111-67	Related correspondence	4

SECTION 6 - EQUIPMENT CALIBRATION

6.01 Calibration Procedures

Equipment Calibration, References and Frequency

All field equipment used during this project will be calibrated and operated in accordance with manufacturer's instructions. Any field equipment used during this project that is not covered by the investigator's standard operating procedures will have a specific calibration and operation instruction sheet prepared for it.

A. General

Standards may be generally grouped into two classifications: primary and secondary. Primary standards include USP and NE drugs, NBS and ASTM materials, and certain designated EPA reference materials. All other standards are to be considered secondary.

B. Testing

1. Primary: No testing is necessary. Do not use if there is any physical indication of contamination or decomposition (i.e. partially discolored, etc.).
2. Secondary: Examine when first received either by comparison to an existing primary, or comparing known physical properties to literature values. The less stable standards will be rechecked at appropriate intervals, usually six months to one year.

C. Records

1. A records book will be maintained for each grouping of standards (i.e. pesticides, metals, etc.)
2. The record kept for each standard will include:
 - a. Name and date received
 - b. Source
 - c. Code or lot number
 - d. Purity
 - e. Testing data including all raw work and calculations
 - f. Special storage requirements
 - g. Storage location
3. These records will be checked periodically as part of the Laboratory Controls Review.

Equipment

A. General

1. Each major piece of analytical laboratory instrumentation used on this project is documented and on file with the analytical laboratory.
2. A form is prepared for each new purchase and old forms will be discarded when the instrument is replaced.

B. Testing

1. Each form details both preventative maintenance activities and the required QA testing and monitoring.
2. In the event the instrument does not perform within the limits specified on the monitoring form, the Laboratory

Manager will be notified and a decision made as to what action to take.

3. If repair is deemed necessary, an "out of order" sign will be placed in the instrument until repairs are effected.

6.02 Calibration Records

A bound notebook will be kept with each instrument, requiring calibration, to record all activities associated with a maintained, QA monitoring and repairs program. Additionally, these records will be checked during periodic equipment review.

SECTION 7 - ANALYTICAL PROCEDURES

7.01 Laboratory Analytical Procedures

The analysis and methods detection limits for standard CLP procedures are given in Table 10 of this section.

The methods associated with:

- Volatile organics in water
 - Volatile organic in soil and sediment
 - Acid extractables and base neutrals
 - Organo chlorine pesticides and PCBs in water and soil samples
- are attached to the end of this section.

But which methods are actually going to be used? You seem to be afraid to clearly state what methods are to be used.

~~Additionally, the laboratory analyzed a variety of matrices for a number of different environmental constituents of concern. Therefore, several documents are referenced which include the procedures employed. The following list itemizes the most widely used documents.~~

1. Standard Methods for the Examination of Water and Wastewater
2. Methods for Chemical Analysis of Water and Wastewater
3. ASTM Annual Book of Standards
4. Code of Federal Regulations
5. NIOSH Manual of Analytical Methods
6. Test Methods for Evaluating Soil Waste, Physical/Chemical Methods

This is only 1. confusing list actual reference for each parameter.

When analyzing samples by the above standardized methods, the accuracy or precision of the data generated by the laboratory is determined through analysis of replicates, spiked samples, synthetic reference standard samples, and/or field or laboratory blanks along

with each set of samples. Any interference are identified and documented.

In general, the methods accuracy is determining by spiking the sample matrix with the analyte at a minimum of three concentration levels. The range of the spiking levels is selected to bracket the concentration of interest. Percent recoveries of the spikes are calculated and are compared with synthetic standards. The methods precision is determined by analyzing a minimum of three replicates at each spiking level. The precision is evaluated by calculating the standard deviation.

The data generated is, whenever possible, input the laboratory base data management system. Analyst's work sheets are filed for one year as a temporary record. When approved and signed, data reports and pertinent information are reported to the client.

The analytical protocols for explosives in soils are presented in Attachment 5. Samples to be analyzed for chlorinated dioxins and dibenzofurans will be analyzed according to the procedure of Smith et al. (1984) or equivalent as presented in Attachment 6.

7.02 Field Procedures

Phase I is completed. ~~Site investigations will be conducted in two phases. Samples collected during the two phases will be shipped, following chain-of-custody procedures to O'Brien & Gere's laboratory for analyses.~~

Field analyses of surface and groundwater will consist of pH, specific conductance and temperature measurements.

SECTION 8 - DATA REDUCTION, VALIDATION, AND REPORTING

8.01 General

O'Brien & Gere's laboratory facilities will perform all testing except for samples split with the U.S.F.W.S., explosives residues by HPLC, CLP Organics, ^{and furnace methods} and PCDD/PCDF analyses. Data reduction and validation will be incorporated into the in-house effort.

8.02 Data Reduction and Reporting

The following data handling procedures are employed at O'Brien & Gere:

- A. Data Production - A Hewlett-Packard Model 5995 and 5993 are used for the positive identification and quantification of sample extracts. Output from the determination is a total ion chromatogram recorded on thermal printer hard copy and cassette tape.
- B. Data Reduction - Output from the GC/MS unit is digitized, stored in memory on cassette tape and processed for presentation in three formats:
 - 1) A real-time total multiple ion mass chromatogram.
 - 2) A post-run integration report contains the following:
 - a. Retention time
 - b. Response factor
 - c. Primary, secondary, and tertiary ion with their corresponding abundance
 - d. Quantitation ion

e. Reference library name

f. Concentration

- 3) A visual comparison of the subject mass spectral output to the library compound.

C. Data Transcription - The post integration report contains the following:

- 1) Listing of all compounds.
- 2) Relative retention times.
- 3) Relative response factor to their internal standards.
- 4) Concentration of compounds, surrogate and internals.

Quality Control/Quality Assurance data such as resolution and calibration standards and DFTPP spectra are also processed and stored in the above manner.

D. Data Verification - The processed transcribed information and the hard copied raw data are now evaluated by the Group Leader to verify the validity of the data and determine whether reinjection or additional cleanup steps are required. The results of the evaluation are recorded in a notebook and inputted into the Sample Status File.

E. Distribution - Following final review the GC/MS Group Leader and Manager of Analytical Services, the results of the analytical determination are shipped to the Contractor. The format used for presentation of data are the presented in the IFB forms. Additional data such as copies of raw data and chromatograms are provided upon request.

F. In-House Storage - Results of all analytical determinations are stored in the RTE6 computer. Raw data tapes are logged into the computer on a separate file and listed by tape number and its contents. The data tapes are stored indefinitely. Should a request be made for a particular raw data tape, the tape is copied and the copy is kept in the archive while the original is sent to the Contractor. All notebooks are also archived and stored in the O'Brien & Gere Central File.

Reporting

Once a sample has been tagged and input into the laboratory data management system, we have the ability to determine its exact status. With the available maintenance programs, and tracking forms, the group leaders can trace the progress of one sample or an entire group of samples. Therefore, a client is able to receive partial data before the entire program is complete.

For a program that covers the course of several months or years, it is imperative that interim reports be submitted. It is anticipated that turnaround for a batch of samples will be 40 days from sample arrival. The RTE6 computer system, with the Aquarius software will generate a final report following injection and data evaluation. Therefore, if specific sample information is required prior to submission of the case, we would be able to satisfy EPA's needs.

Of course there may be certain instances where faster turnaround would be dictated and we shall make every attempt to meet

those needs. Our past experience on programs of this size have proven our capability to supply information in a timely manner.

8.03 Data Validation

Prior to submittal of the data to the Project Manager for his review, data will be validated by the individual laboratory group leaders and/or Manager.

The validation process by group leaders will include the review of spike recoveries, surrogate recovery, comparability of duplicate analysis and field blank integrity. Additionally, the group leaders will check for the adherence to accuracy and precision criteria, unusually high or low parameter values and possible transmittal errors.

Field data ^{what do you mean by field data?} will be reviewed by the Quality Assurance ^{officer?} Manager (QAM). The QAM will critique the field data using the same guidelines where required, as outlined above.

The Quality Assurance ^{officer?} Manager will also perform validation of the data from all laboratories. ^{Is this the laboratory SAM or MR blank?}

The requirements to be checked in validation, in order, are as follows:

- I. Sample Holding Times
- II. Calibration
 - a. Initial Calibration and Calibration Verification
 - b. Continuing Calibration Verification
 - c. Calibration Blank
- III. Blanks
 - a. Laboratory preparation blank

- b. Field blank
- c. Procedural Blank
- IV. Interference Check Sample Analysis
- V. Laboratory Control Sample Analysis
- VI. Specific Sample Results
 - a. Duplicate Sample Analysis
 - b. Spiked Sample Analysis
 - c. AA/QC Analysis
 - 1. Duplicate Injections
 - 2. Analytical Spikes
 - d. ICP QC Analysis
 - e. Sample Result Verification
- VII. Field and Other QC
- VIII. Quarterly Submissions
- IX. Overall Case (Batch) Assessment

The reviewer will compare what was actually performed by the laboratory to the requirements of the protocols and program objectives. The intent is to review all the deliverables for completeness and all the raw data anomalies.

↑
*Suggest they reference methods
used by CRL.*

SECTION 9 - INTERNAL QUALITY CONTROL PROCEDURES

9.01 Quality Control/Quality Assurance Objectives

The quality control objectives for the project are listed with each matrix in Table 10. The requirements for each group of compounds is different, therefore the listing identify the frequency and control limits for acceptability. Upon completion of analysis the results of quality control data will be reviewed to verify compliance with the criteria listed. The goal is to achieve compliance with the criteria, 88% completeness on this matrix spike and matrix spike duplicate. When results are reported to the project team, quality control data will be included in the package for everyones review. This will include the analysis of EPA standard reference materials where available to verify initial calibration of non CLP analysis. The criteria for acceptance will be $\pm 10\%$ of known values. Matrix spikes will monitor the methodology and discoveries will be compared to Exhibit E of the WA-85-177 CLP protocols. Matrix spike duplicates will be incorporated to be an indicator of the precision of sample results. The relative percent difference calculations will be compared to Exhibit E of the CLP protocol.

9.02 Field Sampling Quality Control

Field sampling crews will always be under the direct supervision of a crew chief with a minimum of a Bachelor's degree and five years sampling experience. New employees will be assigned to an experienced staff member and work under his/her direction.

Bound log books and appropriate data sheets will be used to document the collection of samples so that any individual sample can be traced back to its point of origin; sampler and sampling equipment.

Duplicate samples will be collected at the same time, employing the same procedures, equipment and containers as the scheduled sample. Additionally, duplicate samples will be packaged and shipped to the laboratory in the same manner as the required sample.

As specified in Section 8 of this QAPP the QAM will periodically review the results of the duplicate analyses and advise the Project Manager of any problems.

9.03 Field Analytical Procedures Quality Control

Field measurements of pH, temperature and specific conductance will be taken on water samples only. The pH meter will be checked against two known standard pH buffers (7 and 10) before and after each days use.

Temperature measurements will be made with a mercury-filled celsius thermometer. As a minimum, the thermometer will have a scale marked for every 0.1C, with marking etched on the capillary glass. Field operations will require a thermometer with a protective case to prevent breakage. The thermometer will be checked against a precision thermometer certified by the National Bureau of Standards (NBS) periodically.

Conductivity reading will be made with a portable specific conductivity meter. The meter will be calibrated against a 0.010 normal potassium chloride solution (KCL) at least once per day.

SECTION 10 - AUDIT PROCEDURES

well they?
I don't think they have personnel to audit lab procedures. Dick & I'll may audit field procedures. However, QAO will have to audit our own analytical procedures with oversight by

The O'Brien & Gere Project Manager, the Columbia National Fisheries QC/QA Representative and the Refuge Manager will monitor and audit the performance of the QA procedures listed in this plan. They will conduct field and office audits.

The QAO from USEPA, Region V will conduct a systems audit of the laboratories for Phase II analytical parameters, ~~if deemed necessary~~. Procedures for the audits will be established by the QAO prior to such audit. Performance evaluation samples will also be provided by USEPA to appropriate laboratories.

O'Brien & Gere has designated a QA Officer as indicated in Figure 3 (Section 2.02). A performance audit, consisting of analysis of appropriate blanks, fortified samples and standard solutions will be performed prior to initiation of Phase II. O'Brien & Gere's QA Officer will maintain a record of such audits and will inform the FWS of significant deviations from established control limits. These audits will test not only the total system's response, but inherently all major measurement methods.

O'Brien & Gere's QA Officer will report to the Project Manager and the FWS the result of assessment of: the accuracy, precision and completeness of the data, results of the performance and system audits, and any problems encountered in the analytical procedures. The QA Officer, in conjunction with the analyst, analyst's supervisor, and Project Manager will formulate recommendations to correct any deficiency in the analytical protocol or data. These corrective measures will be in

accord with ongoing good laboratory practices and the overall Quality Assurance Program.

SECTION 11 - PREVENTIVE MAINTENANCE

Preventive maintenance procedures will be carried out on all field equipment in accordance with the procedures outlined by the manufacturer's equipment manuals. Any field equipment used during this project that is not covered by the standard operating procedures will have a specific maintenance instruction sheet prepared for it.

*separate from the
reviewed by the QAM in Section 8?
It seems that the QAM is completing this
review as stated in Section 8.*

SECTION 12 - DATA ASSESSMENT PROCEDURES

The O'Brien & Gere laboratories QA/QC group leader will be responsible for assessing the quality of the data generated. His assessment will be based upon instrument tuning criteria, surrogate recoveries, matrix spikes, matrix spike duplicates, duplicate analysis, and reagent and field blank integrity. *Is this*

The QA/QC group leader will advise the QAO of any data which he believes should be rated as "unacceptable" or "preliminary" along with recommendations for corrective action, if deemed necessary. *This is incorporated into the
sup. chart. QA/QC group leader
QAM (S. 8.2)*

Tentatively identified compounds (TIC's) will be brought to the attention of the Project Manager (PM) who has the responsibility of deciding whether to require additional verification or discard the data. *Section 8 states that
QAM conducts indep.
review.*

The Quality Assurance Officer (QAO) has the responsibility of assessing the quality of the data generated by outside contract laboratories. The QAO will review both the analytical data and QA/QC reports and will report any inconsistencies to the PM along with recommendations concerning the acceptability of the data.

Finally, all analytical data will be submitted to and assessed by the USEPA, Region V and FWS in accordance with their standard procedures.

*It would seem preferable to have the
same group assess both internal +
externally produced data. QAM is preferable.*

*What procedures for the
data assessment will be used?
Should be equivalent to procedures
used by U.S. EPA, CRL,*

SECTION 13 - CORRECTIVE ACTION PROCEDURES

Corrective action procedures that might be implemented from audit results or upon detection of data unacceptability are developed on a case-by-case basis.

The actions may include:

- Reanalyzing samples if holding time requirements have not been exceeded.
- Altering field or handling procedures.
- Resampling.
- Using a different batch of sample containers.
- Recommending an audit of laboratory procedures.
- Accepting data with knowledged level of uncertainty.
- Discard data.

The O'Brien & Gere Project Manager is responsible for initiating the corrective action. / The Regional Resource Contaminants Assessment Coordinator is responsible for approving the corrective action.

The SAM will discuss this with the PM and Contaminants Coordinator.

SECTION 14 - QUALITY ASSURANCE REPORTS

~~For this project, no separate report is anticipated to describe the performance of the data measurement systems or the data quality.~~

Discussions of quality assurance problems and corrective actions taken will be included in the project monthly progress reports. The final RI report and the final FS report will contain separate QA sections that summarize data quality information collected during the project.

1. U.S. EPA, QA report, draft
2. QA report to IUS - summary of data quality and performance - digital model.
3. Report to IUS and U.S. EPA on results of data assessment.

TABLE 1
(Continued)

CRAB ORCHARD REFUGE

SAMPLING SITES

<u>Site #</u>	<u>Type</u>	<u>Name</u>
<u>Group 9</u> 28	Landfill	Water Tower Landfill
<u>Group 10</u> 29	Landfill	Fire Station Landfill
<u>Group 11</u> 32 33	Landfill Surface Soil	Area 9 Landfill Area 9 Building Complex
<u>Group 12</u> 34	Lake	Crab Orchard Lake
<u>Group 13</u> 31	Control*	Refuge Control Site

TABLE 2A

RI/FS ANALYTICAL PARAMETERS

Phase I

1. Purgeable Priority Pollutants
(Screening and Full Analysis)
2. Acid Extractable Priority Pollutants
(Screening and Full Analysis)
3. Base/Neutral Extractable Priority Pollutants
(Screening and Full Analysis)
4. Pesticide/PCB Priority Pollutants
(Screening and Full Analysis)
5. PCB's
6. Metals
 - ICP scan
 - Priority Pollutant Metals by AA Spec
 - Mercury
7. EP Toxicity
8. Cyanide 40
9. Indicators
 - pH (field)
 - Specific Conductance (field)
 - Total Organic Carbon
 - Total Organic Halogens
10. Explosives Residues by HPLC
11. Nitrogen Series: TKN, NH₃N, NO₃N
12. PCDD/PCDF
(Screening and Full Analysis)
13. Cation Exchange Capacity
14. Total Phosphorus
15. Primary and Secondary Drinking Water Standards
16. Percent Solids (for soil/sediments)

TABLE 2B

RI/FS ANALYTICAL PARAMETERS
PHASE II
(to be initiated)

1. ^{USEPA CLP HSL Volatiles} Purgeable Priority Pollutants (Full Analysis) *Reference 2C*
2. ^{CLP HSL B/N/A} Acid Extractable Priority Pollutants (Full Analysis) *(Reference 2C)*
3. ^{CLP HSL} Pesticide/PCBs Priority Pollutants (Full Analysis) *(Reference 2C)*
4. PCB's
5. Metals ^{CLP HSL Metals}
 - Priority Pollutant Metals by AA Spec *(Ref, 2C)*
 - Mercury, Magnesium, Cadmium, Lead Arsenic, *Al, Ni, Cu*
 - Copper, Chromium
6. EP Toxicity (Chromium, Cadmium, Lead)
7. Cyanide 40 *?*
8. Indicators
 - pH (field)
 - Specific Conductance (field)
 - ~~Total Organic Halogens~~ *Not included*
9. Explosives Residues by HPLC
10. ~~Nitrogen Series: TKN, NH₃N, NO₃N~~ *not included*
11. PCDD/PCDF (Screening and Full Analysis)
12. Percent Solids (for soil/sediments)
13. Total Suspended Solids
14. Lipids (Percent)

Base Neutrals
Ref 2C

TABLE 2C
LIST OF CHEMICAL COMPOUNDS FOR ANALYSIS

~~not disulfide~~
trans 1,2 dichloroethene
1,2 dichloroethane
trans 1,3 dichloropropene
~~1,2 trichloroethene~~
styrene

PURGEABLE PRIORITY POLLUTANTS

- | | | |
|---------------------------|------------------------------|----------------------------|
| 1 Chloromethane | 15 1,2-Dichloropropane | 29 1,1 Dichloroethylene |
| 2 Bromomethane | 16 t-1,3-Dichloropropene | 30 t-1,2-Dichloroethylene |
| 3 Dichlorodifluoromethane | 17 Trichloroethene | 31 Bromochloromethane |
| 4 Vinyl chloride | 18 Benzene | 32 Trichloroethylene |
| 5 Chloroethane | 19 Dibromochloromethane | 33 2-Bromo-1-chloropropane |
| 6 Methylene Chloride | 20 1,1,2-Trichloroethane | 34 Tetrachloroethylene |
| 7 Trichlorofluoromethane | 21 c-1,3-Dichloropropene | 35 Acetone |
| 8 1,1-Dichloroethene | 22 2-Chloroethylvinyl ether | 36 Carbon disulfide |
| 9 1,1-Dichloroethane | 23 Bromoform | 37 2-Butanone |
| 10 t-1,1-Dichloroethene | 24 1,1,2,2-Tetrachloroethane | 38 Vinyl acetate |
| 11 Chloroform | 25 Tetrachloroethene | 39 2-Hexanone |
| 12 1,1,1-Trichloroethane | 26 Toluene | 40 4-Methyl-2-pentanone |
| 13 Carbon tetrachloride | 27 Chlorobenzene | 41 Styrene |
| 14 Bromodichloromethane | 28 Ethylbenzene | 42 Total xylenes |

ACID EXTRACTABLE PRIORITY POLLUTANTS

- | | | |
|----------------------|---------------------------|-------------------------------|
| 1 Phenol | 6 2-Nitrophenol | 11 Pentafluorophenol |
| 2 d6-Phenol | 7 4-Nitrophenol | 12 2,4,6-Trichlorophenol |
| 3 2-Fluorophenol | 8 4-Chloro-3-methylphenol | 13 2-Methyl-4,6-dinitrophenol |
| 4 2,4-Dimethylphenol | 9 2,4-Dichlorophenol | 14 Pentachlorophenol |
| 5 2-Chlorophenol | 10 2,4-Dinitrophenol | |

BASE/NEUTRAL PRIORITY POLLUTANTS

- | | | |
|---------------------------------|--------------------------------|---------------------------------|
| 1 1,3-Dichlorobenzene | 17 Acenaphthene | 33 Benzidine |
| 2 1,4-Dichlorobenzene | 18 Dimethyl phthalate | 34 Butyl benzyl phthalate |
| 3 1,2-Dichlorobenzene | 19 2,6-Dinitrotoluene | 35 Bis (2-ethylhexyl) phthalate |
| 4 Hexachloroethane | 20 Fluorene | 36 Chrysene |
| 5 Bis (2-chloroethyl) ether | 21 4-Chlorophenyl phenyl ether | 37 Benzo(a)anthracene |
| 6 Bis (2-chloroisopropyl) ether | 22 2,4-Dinitrotoluene | 38 3,3-Dichlorobenzidine |
| 7 N-Nitrosodi-n-propylamine | 23 1,2-Diphenylhydrazine | 39 Di-n-octylphthalate |
| 8 Nitrobenzene | 24 Diethylphthalate | 40 Benzo(b)fluoranthene |
| 9 Hexachlorobutadiene | 25 N-nitrosodiphenylamine | 41 Benzo(k)fluoranthene |
| 10 1,2,4-Trichlorobenzene | 26 Hexachlorobenzene | 42 Benzo(a)pyrene |
| 11 Isophorone | 27 4-Bromophenyl phenyl ether | 43 Indeno(1,2,3-cd)pyrene |
| 12 Naphthalene | 28 Phenanthrene | 44 Dibenzo(a,h)anthracene |
| 13 Bis (2-chloroethoxy) methane | 29 Anthracene | 45 Benzo(g,h,i)perylene |
| 14 Hexachlorocyclopentadiene | 30 Di-n-butyl phthalate | 46 N-Nitrosodimethyl Amine |
| 15 2-Chloronaphthalene | 31 Fluoranthene | |
| 16 Acenaphthalene | 32 Pyrene | |

PESTICIDES/PCB PRIORITY POLLUTANTS

- | | | |
|-----------------------|-----------------------|------------------|
| 1 Alpha-BHC | 10 Dieldrin | 19 Toxaphene |
| 2 Gamma-BHC (Lindane) | 11 Endrin | 20 Arochlor-1016 |
| 3 Beta-BHC | 12 4,4'-DDD | 21 Arochlor-1242 |
| 4 Delta-BHC | 13 Endosulfan II | 22 Arochlor-1221 |
| 5 Heptachlor | 14 4,4'-DDT | 23 Arochlor-1232 |
| 6 Aldrin | 15 Endosulfan Sulfate | 24 Arochlor-1248 |
| 7 Heptachlor epoxide | 16 Endrin Aldehyde | 25 Arochlor-1254 |
| 8 Endosulfan I | 17 Methoxychlor | 26 Arochlor-1260 |
| 9 4,4'-DDE | 18 Chlordane | 27 Endrin ketone |

not
diff
in
CLP

TABLE 2C *full*
LIST OF CHEMICAL COMPOUNDS FOR ANALYSIS (contd.)

PCDDs/PCDFs

1 Tetra-CDD	5 Octa-CDD	9 Hepta-CDF
2 Penta-CDD	6 Tetra-CDF	10 Octa-CDF
3 Hexa-CDD	7 Penta-CDF	
4 Hepta-CDD	8 Hexa-CDF	

Not in Phase II

EXPLOSIVES RESIDUES BY HPLC

1 RMX	4 1,3 DNB	7 2,4,6 TNT
2 RDX	5 NB	8 2,6 DNT
3 1,3,5 TNB	6 TETRYL	9 2,4 DNT

METALS (ICPs AND PP ATOMIC ABS.)

1 Aluminum	10 Iron	20 Silver
2 Antimony	11 Lead	21 Sodium
3 Arsenic	12 Magnesium	22 Tin
4 Barium	13 Manganese	23 Titanium
5 Cadmium	14 Molybdenum	24 Vanadium
6 Calcium	15 Mercury	25 Zinc
7 Chromium	16 Nickel	
8 Cobalt	17 Potassium	
9 Copper	18 Selenium	

*Drop 3
add 2*

OTHERS

INDIATORS

- 1 pH
- 2 Specific Conductivity
- 3 Total Organic Carbon
- 4 Total Organic Halides

~~NITROGEN SERIES~~

- 1 Ammonia Nitrogen
- 2 Nitrate Nitrogen
- 3 Nitrite Nitrogen
- 4 Total Kjeldahl Nitrogen

CYANIDE

~~CATION EXCHANGE CAPACITY~~

~~TOTAL PHOSPHORUS~~

SAFE DRINKING WATER ACT STANDARDS

Primary Inorganic Chemicals

- 1 Arsenic
- 2 Barium
- 3 Cadmium
- 4 Chromium
- 5 Fluoride
- 6 Lead
- 7 Mercury
- 8 Nitrate
- 9 Silver

Organic Chemicals

- 1 Endrin
- 2 Lindane
- 3 Methoxychlor
- 4 Toxaphene
- 5 2,4-D
- 6 2,4,5-TP Silvex

*ammonia
nitrate/nitrite
chloride*

Secondary Inorganic Chemicals

- 1 Chloride
- 2 Copper
- 3 Iron
- 4 Manganese
- 5 Sodium
- 6 Sulfate
- 7 Zinc
- 8 Corrosivity

TABLE 3

REMEDIAL INVESTIGATION SAMPLING AND ANALYSIS SEQUENCE

<u>Site Category</u>	<u>Recon.</u>	<u>Phase I</u>	<u>Phase II</u>	<u>Contingency</u>
Landfills	Geophysics	Cores - depth composites - screening & full priority pollutants & explosives residuals + ICP metals - Install wells-analyze indicators + metals.	Radial & depth cores and wells for priority pollutants & explosives residuals found in cores & AA metals.	
Surface	Geophysics - locate utilities	Surf. Soils - screening & full priority pollutants and explosive residuals + ICP metals.	Depth soils Radial soils - surf. & depth Runoff - water & sediments & depth profile	
Streams - Waters - Sediments		Upstream/downstream - screening & full priority pollutants & explosive residuals Surf. sed: 2 near shore, 1 near lake - screening & full priority pollutants + expl. + ICP metals	Surf seds - int + depth sed. - priority pollutants found + AA metals	
Ponds - Waters - Sediments - Groundwater		(Same rationale as streams) (Same rationale as streams) Upgradient/downgradient wells (2) - indicators	Depth profile on sediments priority pollutants + expl. found in waters or sed.	Additional wells
Lake - Waters - Sediments - Biota		5 sites; primary & secondary - Drinking Water stds. (None) Sample & freeze	5 biota sites + 5 use sites: anything found in Phase I 5 sites: parameters found in Phase I parameters found in Phase I	
Control Sites - Lake control - Soil & groundwater control - Clean area - Munitions area		(All analyses included at other sites)	Full scans	

*ICP: Metals analysis by Induced Coupled Plasma Spectrophotometry

AA: Metals analysis by Atomic Adsorption Spectrophotometry

SUMMARY OF ANALYSES TO BE PERFORMED

will be
done

Task No. (WORK PLAN)	No. Samples Collected	No. For Screening (Phase I)	Selected <i>Grain size soil classification permeability</i> Full Analyses (Phase I)	Selected ⁽³⁾ Parameters (Phase II)	Field Analyses	Comments
2-B Site Maps	--	--	--	--	--	1"=50' Scale with 1' contours
3-A Geophysical Survey 6 sites	6 sites --	--	--		Terrain Conductivity Magnetometer	EM-31 Meter Used Proton Magneto- meter
3-B Hyrdogeologic Investigations installed during Phase I	9 wells to be	--	--	--	Fire Sta. - 4 wells Acid Pond - 1 well Refuge control-1 well Munciation Control - 1 well Water Tower - 2 wells	2" ID PVC Casing and well screening
3-C Groundwater Sampling and Analyses (1)	16	--	--	See Table 7	Temp, pH and Spec. Conditions <i>not used</i>	Samples will be collected and Analyzed in Phase II
3-D Soil Investigation	328	72(A) 192(B) 27(C) 15(D)	6-(F) 7(G) 9(H)	See Table 7		
3-E Surface Water and Sediment Investigation	36 71	21(A) 5(E) 41(A) 7(D)	10(F) 3(G)	See Table 7		
3-F Biota (2)	30	--	--	See Table 7	Length and Weight	Samples Frozen before shipping. Scheduled for analyses during Phase II.

Note:

The letters in parenthesis under screening and full analysis for Phase I indicate analysis sets (see Table 5).

- (1) Sampling and Analyses of Ground Water scheduled for Phase II
- (2) Fish samples obtained in Phase I, analyses scheduled for Phase II
- (3) Specific details on parameters analysed

Table 5

CONWR

PARAMETER LIST FOR PHASE I ANALYSIS SETS

Sept. 2, 1986

PARAMETERS		ANALYSIS SET							
		A	B	C	D	E	F	G	H
1. Purgeable Priority Pollutants	-Screen	X	-	-	X	-	-	-	-
	-Full Anal.	-	-	-	-	-	X	X	X
2. Acid Extract. Priority Pollutants	-Screen	X	-	-	X	-	-	-	-
	-Full Anal.	-	-	-	-	-	X	X	X
3. Base/Neutral Extract. Prior. Poll.	-Screen	X	-	-	X	-	-	-	-
	-Full Anal.	-	-	-	-	-	X	X	X
4. Pesticide/PCB Priority Pollutants	-Screen	X	-	-	X	-	-	-	-
	-Full Anal.	-	-	-	-	-	X	X	X
5. PCB's		-	X	X	-	-	-	-	-
6. Metals - ICP Scan		X	-	-	X	-	-	-	-
	- Prior. Poll. Metals by AA	-	-	-	-	-	-	-	X
	- Mercury	X	-	-	X	-	-	-	-
7. EP Toxicity Metals		-	-	-	-	-	-	-	-
8. Cyanide		X	-	-	X	-	-	-	X
9. Indicators - pH (field)		X	-	X	X	-	-	-	X
	- Specific Conductance (field)	X	-	X	X	-	-	-	X
	- Total Organic Carbon	X	-	X	X	-	-	-	X
	- Total Organic Halogen	X	-	X	X	-	-	-	X
10. Explosives Residues by HPLC		X	-	-	X	-	-	-	X
11. Nitrogen Series: TKM, NH3, NO3		X	-	X	X	-	-	-	X
12. PCDD/PCDF	-Screen	-	-	X	X	-	-	-	-
	-Full Anal.	-	-	-	-	-	-	X	X
13. Cation Exchange Capacity		-	-	X	-	-	X	X	-
14. Total Phosphorus		X	-	-	X	-	-	-	X
15. Primary & Secondary Drinking Water Stds.		-	-	-	-	X	-	-	-
16. Percent Solids (on soil/sed only)		X	X	X	X	-	X	X	X

NOTE: SETS F & G are full analysis of parameters screened in SETS A & D resply.

SET H is full analysis of selected samples instead of SET D

CONWR

PHASE I SAMPLING & ANALYSIS SUMMARY

Sept. 2, 1986

SITE NO.	SAMPLE TYPE	WATER NO.OF ANAL. SAMPL TYPE	SOILS NO.OF ANAL. SAMPL TYPE	SEDIMENTS NO.OF ANAL. SAMPL TYPE
3	AREA 11 SOUTH LANDFILL	0 -	3 A 1 F	1 A 1 D
4	AREA 11 NORTH LANDFILL	0 -	1 D	1 A 1 F
5	AREA 11 ACID POND	1 A	1 A	1 A 1 F
7A	D AREA NORTH LAWN	0 -	16 A 1 F	0 -
11A	P AREA NORTH	0 -	4 A	4 A 1 F
7	D AREA SOUTHEAST DRAINAGE	1 A	0 -	1 A
8	D AREA SOUTHWEST DRAINAGE	1 A	0 -	1 A
9	D AREA NORTHWEST DRAINAGE	1 A	0 -	1 A
10	WATERWORKS NORTH DRAINAGE	1 A	0 -	1 D 1 G
11	P AREA SOUTHEAST DRAINAGE	1 A	0 -	1 A 1 F
20	D AREA SOUTH	0 -	0 -	1 A 1 F
12	AREA 14 LANDFILL	0 -	1 D	1 A 1 G
13	AREA 14 CHANGE HOUSE SITE	0 -	6 A	0 -
14	AREA 14 SOLVENT STORAGE	2 A	0 -	2 A 1 F
15	AREA 7 PLATING POND	1 A	0 -	1 A
16	AREA 7 INDUSTRIAL SITE	2 A	7 A 2 D 1 F 1 G	3 A 1 F
17	JOB CORPS LANDFILL	2 A	5 A 2 D 2 G	0 -
18	AREA 13 LOADING PLATFORM	0 -	4 A 1 F	0 -

Table 6 (pg 2 of 3)

CONWR

PHASE I SAMPLING & ANALYSIS SUMMARY

Sept. 2, 1986

SITE NO.	SAMPLE TYPE	WATER NO.OF ANAL. SAMPL TYPE	SOILS NO.OF ANAL. SAMPL TYPE	SEDIMENTS NO.OF ANAL. SAMPL TYPE
19	AREA 13 BUNKER 1-3	0 -	5 A 1 P	0 -
30	MUNITIONS CONTROL SITE	0 -	1 D 1 G	0 -
21	SOUTHEAST CORNER FIELD	0 -	4 A 1 P	0 -
22	OLD REFUGE SHOP	1 A	0 -	1 A 1 P
24	PEPSI-WEST	1 A	0 -	1 A 1 P
25	C.O.CREEK AT MARION LP	3 A	0 -	2 A 1 D 1 G
26	C.O.CREEK BELOW MARION STP	2 A	0 -	2 A
27	C.O.CREEK BELOW 157 DREDGE	1 A	0 -	1 D
28	WATER TOWER LANDFILL	0 -	11 A 1 D 1 G	0 -
29	FIRE STATION LANDFILL	0 -	5 A 2 D 1 G	0 -
32	AREA 9 LANDFILL	0 -	1 A 8 B 27 C 9 H	15 A 3 D
33	AREA 9 BUILDING COMPLEX	0 -	184 B 4 D	0 -
35	AREA 9 EAST WATERWAY	0 -	0 -	1 A 1 P
34	CRAB ORCHARD LAKE	5 B	0 -	0 -
31	REFUGE CONTROL SITE	0 -	1 D 1 G	0 -
TOTAL NUMBER OF ANALYSES		26	328	61 415

Table 6 (pg 3 of 3)

CONWR

PHASE I SAMPLING & ANALYSIS SUMMARY

Sept. 2, 1986

SUMMARY BY ANALYSIS SETS

NO. OF ANALYSES	SCREENING					SUB-TOTAL	FULL ANALYSIS			TOTAL
	A	B	C	D	E		F	G	H	
WATER	21	0	0	0	5	26	0	0	0	26
SOILS	72	192	27	15	0	306	6	7	9	328
SEDIMENTS	41	0	0	7	0	48	10	3	0	61
SUB-TOTAL	134	192	27	22	5	380	16	10	9	415
QA/QC - WATER	1	0	0	0	0	1	0	0	0	1
QA/QC - SOIL	12	31	4	6	0	53	1	2	2	58
QA/QC - SEDIMENT	7	0	0	1	0	8	2	1	0	11
QA/QC - BLANKS	9	0	0	1	0	10	0	2	1	13
QA/QC - TOTAL	29	31	4	8	0	72	3	5	3	83
TOTAL	163	223	31	30	5	452	19	15	12	498

CONWR

TABLE 7 (page 1 of 15)

Sept. 2, 1986

PHASE II ANALYSIS

SITE #10 : WATERWORKS NORTH DRAINAG

PARAMETERS

WATER NUMBER OF SAMPLES
WELL SOILS SEDIMENT

- ↓
1. Purgeable Prior. Poll.
 2. Acid Extract. Prior. Poll.
 3. Base/Neutral Prior. Poll.
 4. Pesticide/PCB Prior. Poll.
 5. PCB's
 6. Metals - All metals by AA ← *As per table is meant by this*
 - Mercury
 - Cadmium
 - Chromium
 - Magnesium
 - Lead
 - Arsenic
 - Copper
 7. EP Toxicity - Cr
 - Cd, Cr, Pb
 8. Cyanide
 9. Indicators - pH
 10. Explosives by HPLC
 11. Lipids
 12. PCDD/PCDF
 13. Total Phosphorus
 14. Percent Solids (soil/sed)

As per sample is not in for 19.

Identify blanks & duplicates

PHASE II ANALYSIS

SITE #11 : P AREA SOUTHEAST DRAINAG

PARAMETERS	NUMBER OF SAMPLES		
	WATER	WELL	SOILS SEDIMENT
1. Purgeable Prior. Poll.			
2. Acid Extract. Prior. Poll.			
3. Base/Neutral Prior. Poll.			
4. Pesticide/PCB Prior. Poll.			
5. PCB's			
6. Metals - All metals by AA			
- Mercury	1		1
- Cadmium			
- Chromium			
- Magnesium			
- Lead			
- Arsenic			
- Copper			
7. EP Toxicity - Cr			
- Cd, Cr, Pb			
8. Cyanide	1		
9. Indicators - pH	1		
10. Explosives by HPLC			
11. Lipids			
12. PCDD/PCDF			
13. Total Phosphorus			
14. Percent Solids (soil/sed)			

PHASE II ANALYSIS

SITE #14 : AREA 14 SOLVENT STORAGE

PARAMETERS	NUMBER OF SAMPLES		
	WATER	WELL	SOILS SEDIMENT
1. Purgeable Prior. Poll.	1		1
2. Acid Extract. Prior. Poll.	1		1
3. Base/Neutral Prior. Poll.	- Analyzed together in CLP;		
4. Pesticide/PCB Prior. Poll.			
5. PCB's			
6. Metals - All metals by AA			
- Mercury			
- Cadmium			
- Chromium			
- Magnesium			
- Lead			
- Arsenic			
- Copper			
7. EP Toxicity - Cr			
- Cd, Cr, Pb			
8. Cyanide			
9. Indicators - pH	1		1
10. Explosives by HPLC			
11. Lipids			
12. PCDD/PCDF			
13. Total Phosphorus			
14. Percent Solids (soil/sed)			1

PHASE II ANALYSIS

SITE #15 : AREA 7 PLATING POND

PARAMETERS		NUMBER OF SAMPLES WELL SOILS SEDIMENT
1. Purgeable Prior. Poll.		✓ Install 2 p.c.m. b.s. + install ground water monitoring wells down to aquifer
2. Acid Extract. Prior. Poll.		X ✓
3. Base/Neutral Prior. Poll.		1
4. Pesticide/PCB Prior. Poll.		1
5. PCB's		1
6. Metals - All metals by AA		1
- Mercury		1
- Cadmium		1
- Chromium		1
- Magnesium		1
- Lead		1
- Arsenic		1
- Copper		1
7. EP Toxicity - Cr		1
- Cd, Cr, Pb		Mold made to 2 purgeable by hand 1
8. Cyanide		1
9. Indicators - pH		1
10. Explosives by HPLC		1
11. Lipids		
12. PCDD/PCDF		
13. Total Phosphorus		1
14. Percent Solids (soil/sed)		1 ← I- sampling in <u>aquifer</u>

possibly more work needed.

possibly also in the large ls, BN &
interbedded with the argill. ls. & sh. in
vicinity of loc 16.

PHASE II ANALYSIS

SITE #16 : AREA 7 INDUSTRIAL SITE

PARAMETERS	NUMBER OF SAMPLES		
	WATER	WELL	SOILS SEDIMENT
1. Purgeable Prior. Poll.	1		1
2. Acid Extract. Prior. Poll.			
3. Base/Neutral Prior. Poll.	1		1
4. Pesticide/PCB Prior. Poll.	1		1 <i>pest/PCB's</i>
5. PCB's			<i>present</i>
6. Metals - All metals by AA			
- Mercury			
- Cadmium			
- Chromium			
- Magnesium	.1		1
- Lead	1		1
- Arsenic	1		1
- Copper			
7. EP Toxicity - Cr			
- Cd, Cr, Pb			
8. Cyanide			
9. Indicators - pH	1		1
10. Explosives by HPLC			
11. Lipids			
12. PCDD/PCDF			
13. Total Phosphorus			
14. Percent Solids (soil/sed)			1

PHASE II ANALYSIS

SITE #17 : JOB CORPS LANDFILL

PARAMETERS	NUMBER OF SAMPLES				
	WATER	WELL	SOILS	SEDIMENT	
1. Purgeable Prior. Poll.	2	3,1			1
2. Acid Extract. Prior. Poll.					1
3. Base/Neutral Prior. Poll.	2	3,1			1
4. Pesticide/PCB Prior. Poll.	2	3,1			1
5. PCB's	X	3,1	35,12	6	
6. Metals - All metals by AA		3,1			1
- Mercury		3,1			
- Cadmium	2	3,1	35,12	6	
- Chromium					
- Magnesium					
- Lead	2	3,1	35,12	6	
- Arsenic	2	3,1			
- Copper	2	3,1			
7. EP Toxicity - Cr					
- Cd, Cr, Pb					1
8. Cyanide		4			1
9. Indicators - pH	2	3,1	35,12	6	
10. Explosives by HPLC	2	3,1	- ,12	6	
11. Lipids					
Grain Size					4
12. PCDD/PCDF					
13. Total Phosphorus					
14. Percent Solids (soil/sed)				6	
field permeability					

NOTE: Total of 4 well water samples
35 surface and 12 core soil s

Will need modification in
installation proc. Add one deep boring &
then adjust new location, if needed.

PHASE II ANALYSIS

SITE #30: MUNITIONS CONTROL SITE

PARAMETERS	NUMBER OF SAMPLES			
	WATER	WELL	SOILS	SEDIMENT
1. Purgeable Prior. Poll.	1			
2. Acid Extract. Prior. Poll.	1			
3. Base/Neutral Prior. Poll.	1		1	
4. Pesticide/PCB Prior. Poll.	1			
5. PCB's				
6. Metals - All metals by AA	1			
- Mercury				
- Cadmium				
- Chromium				
- Magnesium				
- Lead				
- Arsenic				
- Copper				
7. EP Toxicity - Cr				
- Cd, Cr, Pb				
8. Cyanide	1			
9. Indicators - pH	1		1	
10. Explosives by HPLC				
11. Lipids				
12. PCDD/PCDF				
13. Total Phosphorus				
14. Percent Solids (soil/sed)			1	

PHASE II ANALYSIS

SITE #22 : OLD REFUGE SHOP

PARAMETERS	NUMBER OF SAMPLES		
	WATER	WELL	SOILS SEDIMENT
1. Purgeable Prior. Poll.		1	
2. Acid Extract. Prior. Poll. <i>f together</i>		1	1,0
3. Base/Neutral Prior. Poll.			
4. Pesticide/PCB Prior. Poll.			
5. PCB's			
6. Metals - All metals by AA		1	
- Mercury			
- Cadmium		X	1,3
- Chromium		X	1,3
- Magnesium			
- Lead			-,3
- Arsenic			
- Copper			
7. EP Toxicity - Cr			
- Cd, Cr, Pb			-,3
8. Cyanide		1	1,3
9. Indicators - pH		1	1,3
10. Explosives by HPLC			
11. Lipids			
12. PCDD/PCDF			
13. Total Phosphorus			
14. Percent Solids (soil/sed)			1 1,3

NOTE: Total of 4 sediment samples

PHASE II ANALYSIS

SITE #25 : C.O. CREEK AT MARION LF

PARAMETERS	NUMBER OF SAMPLES		
	WATER	WELL	SOILS SEDIMENT
1. Purgeable Prior. Poll.			
2. Acid Extract. Prior. Poll.			
3. Base/Neutral Prior. Poll.			
4. Pesticide/PCB Prior. Poll.			
5. PCB's			
6. Metals - All metals by AA			
- Mercury			
- Cadmium			
- Chromium			
- Magnesium			
- Lead			
- Arsenic			
- Copper			
7. EP Toxicity - Cr			
- Cd, Cr, Pb			
8. Cyanide			1
9. Indicators - pH			1
10. Explosives by HPLC			
11. Lipids			
12. PCDD/PCDF			
13. Total Phosphorus			
14. Percent Solids (soil/sed)			1

PHASE II ANALYSIS

SITE #28 : WATER TOWER LANDFILL

PARAMETERS	NUMBER OF SAMPLES			
	WATER	WELL	SOILS	SEDIMENT
1. Purgeable Prior. Poll.		3		1
2. Acid Extract. Prior. Poll.				
3. Base/Neutral Prior. Poll.				
4. Pesticide/PCB Prior. Poll.		3		
5. PCB's			4	
6. Metals - All metals by AA		3		1
- Mercury				
- Cadmium				
- Chromium				
- Magnesium			4	
- Lead			4	
- Arsenic			4	
- Copper			4	
7. EP Toxicity - Cr				
- Cd, Cr, Pb				
Ammonia, nitrate, etc. If sampling in aquifer.				
8. Cyanide		3	4	1
9. Indicators - pH		3	4	1
10. Explosives by HPLC				4
Small size,				
11. Lipids				
field perm,				
12. PCDD/PCDF				
13. Total Phosphorus				
14. Percent Solids (soil/sed)			4	

will probably need additional monitoring well.

add one deep boring and adjust new location if needed.

Must submit safety plan for test pits.

PHASE II ANALYSIS

SITE #29 : FIRE STATION LANDFILL

PARAMETERS	NUMBER OF SAMPLES			D. S. M. H.
	WATER	WELL	SOILS SEDIMENT	
1. Purgeable Prior. Poll.		2, 2		1
2. Acid Extract. Prior. Poll.				
3. Base/Neutral Prior. Poll.				
4. Pesticide/PCB Prior. Poll.		2, 2		1
5. PCB's				
6. Metals - All metals by AA		2, 2		1
- Mercury		2, 2		
- Cadmium		2, 2		
- Chromium				
- Magnesium		2, 2	13	
- Lead		2, 2	13	
- Arsenic		2, 2		
- Copper		2, 2		
7. EP Toxicity - Cr				
- Cd, Cr, Pb				
<i>Ammonia, nitrate, nitrite</i>				
8. Cyanide		4		1
9. Indicators - pH		2, 2	13	1
10. Explosives by HPLC				
<i>Grain size permeability</i>				4
11. Lipids				
12. PCDD/PCDF				
13. Total Phosphorus				
14. Percent Solids (soil/sed)		2, 2	13	

NOTE: Total of 4 well water samples

will probably have to install an additional monitoring well. Install a deep boring and report monitoring in this location if needed.

PHASE II ANALYSIS

SITE #32: AREA 9 LANDFILL

PARAMETERS	NUMBER OF SAMPLES			
	WATER	WELL	SOILS	SEDIMENT
1. Purgeable Prior. Poll.		5		5
2. Acid Extract. Prior. Poll.		5		5
3. Base/Neutral Prior. Poll.		5		5
4. Pesticide/PCB Prior. Poll.		5		5
5. PCB's				42
6. Metals - All metals by AA		5		
- Mercury			24	
- Cadmium				
- Chromium			24	
- Magnesium				
- Lead			24	42
- Arsenic				
- Copper				
7. EP Toxicity - Cr				
- Cd, Cr, Pb				
8. Cyanide		5		
9. Indicators - pH		5		
10. Explosives by HPLC				
Grain size, permeability		4		
11. Lipids				
12. PCDD/PCDF				
13. Total Phosphorus				
14. Percent Solids (soil/sed)			24	42

If
unable to
validate
previous
data

will def
due to p... data

May need to relocate monitoring wells.

Reanalyze 24 Phase I ...
Pt, Cr + Hg

PHASE II ANALYSIS

SITE #33 : AREA 9 BUILDING COMPLEX

PARAMETERS	NUMBER OF SAMPLES		
	WATER	WELL	SOILS SEDIMENT
1. Purgeable Prior. Poll.		3	3
2. Acid Extract. Prior. Poll.		3	3
3. Base/Neutral Prior. Poll.		3	3
4. Pesticide/PCB Prior. Poll.		3	3
5. PCB's		X	151
6. Metals - All metals by AA		3	3
- Mercury		X	
- Cadmium		X	
- Chromium		X	
- Magnesium		X	
- Lead		X	
- Arsenic		X	
- Copper		X	
7. EP Toxicity - Cr			
- Cd, Cr, Pb			
Ammonia, Nitrate, Fluoride			
8. Cyanide		3	
9. Indicators - pH		3	
10. Explosives by HPLC			
11. Lipids			
12. PCDD/PCDF			
13. Total Phosphorus			
14. Percent Solids (soil/sed)			151

the report to report
 1/23/86
 1/23/86

PHASE II ANALYSIS

SITE #34 : CRAB ORCHARD LAKE

PARAMETERS	WATER	WELL	SEDIMENT	BIOTA
1. Purgeable Prior. Poll.	2,5		-,2	
2. Acid Extract. Prior. Poll.	2,5		-,2	
3. Base/Neutral Prior. Poll.	10,5		8,2	
4. Pesticide/PCB Prior. Poll.	10,5		8,2	30
5. PCB's (low level)	-,5 ✓			
nitrosamines (low level)	10,5			
6. Metals - All metals by AA	10,5		8,2	
- Mercury	14,5		8,2	30
- Cadmium	14,5			30
- Chromium				
- Magnesium				
- Lead	14,5			30
- Arsenic	14,5		8,2	
- Copper	10,5			
7. EP Toxicity - Cr				
- Cd, Cr, Pb				
8. Cyanide	10,5		8,2	
9. Indicators - pH	10,5		8,2	
10. Explosives by HPLC			-,2	
Ammonia, nitrate, chloride	10,5			
11. Lipids				30
12. PCDD/PCDF			-,2	
13. Total Phosphorus				
14. Percent Solids (soil/sed)			8,2	

NOTE: Total of 15 water samples (5 Biota (fish) samples include

and the *Thymus*.

PHASE II ANALYSIS

SITE #31 : REFUGE CONTROL SITE

PARAMETERS	NUMBER OF SAMPLES		
	WATER	WELL	SOILS SEDIMENT
1. Purgeable Prior. Poll.		1	
2. Acid Extract. Prior. Poll.		1	
3. Base/Neutral Prior. Poll.		1	
4. Pesticide/PCB Prior. Poll.		1	
5. PCB's		1	
6. Metals - All metals by AA		1	
- Mercury			
- Cadmium			
- Chromium			
- Magnesium			
- Lead			
- Arsenic			
- Copper			
7. EP Toxicity - Cr			
- Cd, Cr, Pb			
8. Cyanide		1	
9. Indicators - pH		1	
10. Explosives by HPLC			
11. Lipids			
12. PCDD/PCDF			
13. Total Phosphorus			
14. Percent Solids (soil/sed)			

Q mistaken
OK

Q

Q

Blank & Duplicate Samples
have not been identified

SUMMARY OF BIOTA SAMPLING FOR PHASE II ANALYSIS

CRAB ORCHARD LAKE SITE No.	NUMBER OF FISH PER COMPOSITE		SPECIES
1		5	Carp
		5	Bass
	*	5	Bass
		5	Bullhead
	**	5	Bullhead
		2	Catfish
2	**	5	Carp
	*	5	Carp
		5	Bass
		5	Bullhead
	*	5	Bullhead
		5	Catfish
3		5	Carp
	*	5	Carp
	**	5	Bass
		5	Bullhead
	*	5	Bullhead
4	**	5	Carp
		5	Bass
	*	5	Bass
		5	Bullhead
	*	5	Bullhead
		4	Catfish
Lake Control		5	Carp
	*	5	Carp
	**	3	Bass
	*	5	Bass
		5	Bullhead
	*	5	Bullhead
		3	Catfish

NOTES (*) = Duplicate composites for OB&G analysis
 (**) = Duplicate composites for FWS analysis

CONVR

TABLE 7C

Sept. 2, 1986

PHASE II ANALYSIS SUMMARY

NO OF ANALYSIS, DETECTION LEVELS AND REFERENCE BY PARAMETERS

PARAMETERS	WATER			WELL			SOIL			SEDIMENT			BIOTA			TOTAL
	No. of Analysis	Det. Level (ppb)	Pg.no.in Table 10	No. of Analysis	Det. Level (ppb)	Pg.no.in Table 10	No. of Analysis	Det. Level (ppb)	Pg.no.in Table 10	No. of Analysis	Det. Level (ppb)	Pg.no.in Table 10	No. of Analysis	Det. Level (ppb)	Pg.no.in Table 10	No. of Analysis
1. Purgeable Prior. Poll.	4	10	1	8	10	1				3	10					15
2. Acid Extract. Prior. Poll.	1	10-50	4	3	10-50	4	1	330-1600	11	3	330-1600	11				8
3. Base/Neutral Prior. Poll.	17	10-50	2	8	10-50	2	2	330-1600	9	15	330-1600	9				42
4. Pesticide/PCB Prior. Poll.	10	.05-1	3	7	.05-1	3				10	80-160	10	30	50	16	57
5. PCB's	7	5 ppt	3	7	5 ppt	3	91	80-160	10	40	80-160	10				153
6. Metals - All metals by AA	10	10-5000	5	7	10-5000	5				8	1-500ppm	12				25
- Mercury - Cold Vap.	6	0.2	5				*	20	12	*	20	12	30	20	17	36
- Cadmium - Flame							48	500	12	10	500	12	30	10	17	88
- Furnace	5	0.1	5	8	0.1	5										13
- Chromium - Flame				5	50	5	1	5000	12	5	5000	12				11
- Magnesium - Flame	1	10	5	6	10	5	17	1000	12	1	1000	12				25
- Lead - Flame							88 *	10000	12	52	10000	12	30	10000	17	160
- Furnace	6	1.0	5	10	1.0	5										16
- Arsenic - Furnace	6	1.0	5	10	1.0	5	4	100	12	1	100	12				21
- Copper - Flame							4	2000	12							4
- Furnace	2	1.0	5	11	1.0	5										13
7. BP Toxicity - Cr										1	1000	12				1
- Cd, Cr, Pb										3	1000,2	12				3
8. Cyanide	12	50	6	8	50	6	17 *	2000	13	19 *	2000	13				56
9. Indicators - pH	21	-	6	22	-	6	67	--	13	29	--	13				139
10. Explosives by NPLC	2	0.4-2.0		4	0.4-2.0		12	500	15	8	500	15				26
11. Lipids													30	100 ppm	10	30
12. PCDD/PCDF							2	0.02-0.2	14							2
13. Total Phosphorus — ?				1	10	6				2	1000	16				3
14. Percent Solids (soil/sed)							242	0.1%	13	71	0.1%	13				313

NOTE: * Additional Phase I samples have been rescheduled for analysis
 All priority pollutants are full analysis (CLP)
 Metals analyses for well waters include unfiltered and filtered

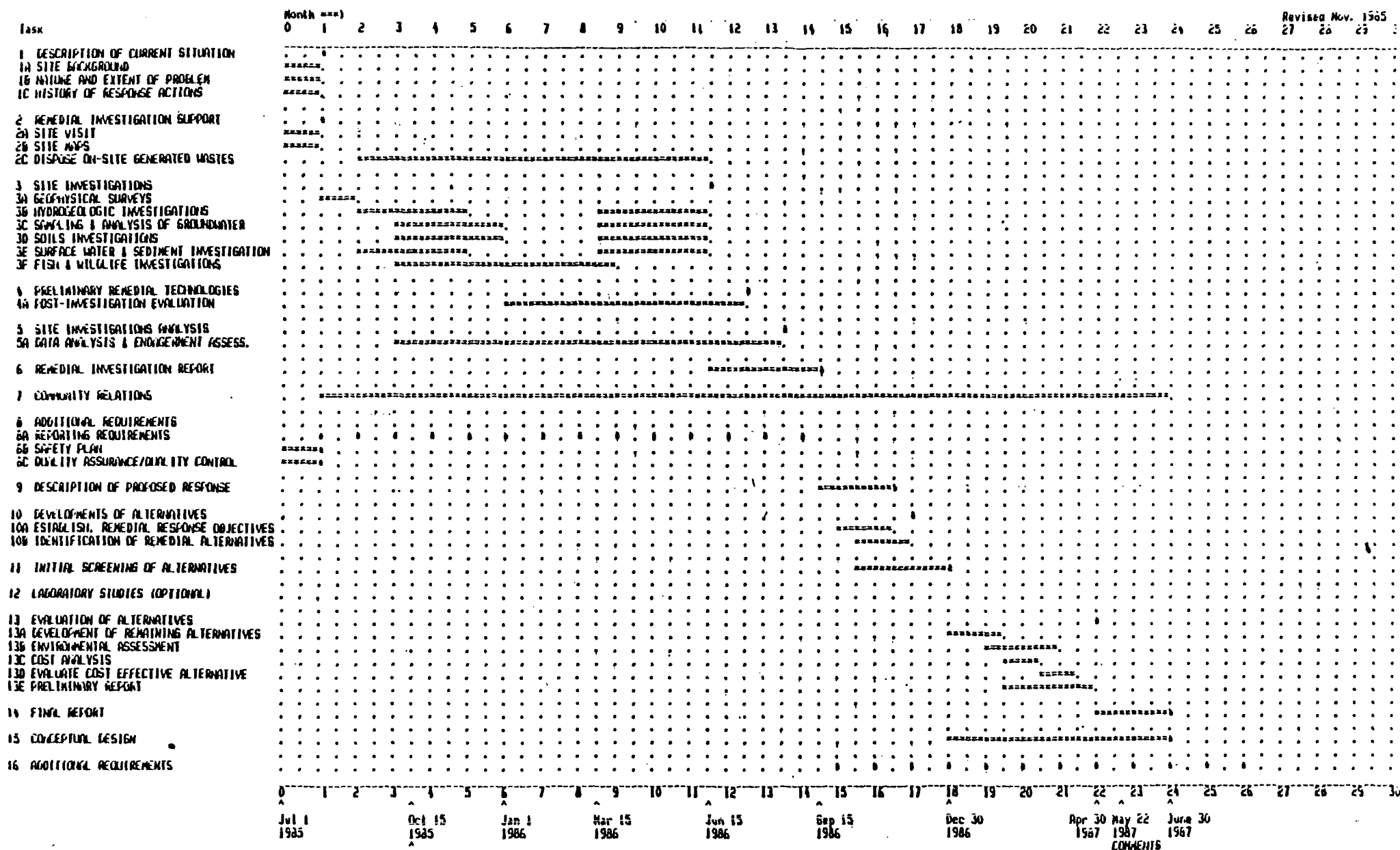
need to diff
 full analysis methods from
 others (indicated),

2. Need to diff nitroamines, & above
 sample

3. Need to diff samples for low
 analyses PCB's,

CRAB ORCHARD NATIONAL WILDLIFE REFUGE

Revised Project Schedule



Subtask Durations ***
Task Deliverables *

TABLE 8
FUNCTIONAL ACTIVITIES

<u>Task/Activity</u>	<u>Responsible Company</u>	<u>Where Performed</u>
<u>Task 1</u> - Description of Current Situation	O'Brien & Gere Engineers, Inc.	Main Office, Syracuse, New York
<u>Task 2</u> - Remedial Investigation Support		
Support - A - Site Visit	O'Brien & Gere Engineers, Inc.	On-Site
B - Site Maps	O'Brien & Gere Engineers, Inc.	Main Office, Syracuse, New York
<u>Task 3</u> - Site Investigations		
A - Geophysical Surveys	O'Brien & Gere Engineers, Inc.	On-Site
B - Hydrogeologic Investigations	O'Brien & Gere Engineers, Inc.	On-Site
- Installation of Monitoring Wells	Professional Service Industries, Inc. with O'Brien & Gere Engineers, Inc. Supervising	On-Site
C - Groundwater: Sampling Analyses	O'Brien & Gere Engineers, Inc. O'Brien & Gere Laboratories, Inc. Rocky Mountain Environmental Testing & Certification (ETC)	On-Site Laboratory - Syracuse, New York Denver, Colorado Laboratory - Edison, New York
D - Soil Investigation: Sampling Analyses	O'Brien & Gere Engineers, Inc. O'Brien & Gere Laboratories, Inc. Roy F. Weston, Inc.	On-Site Laboratory, Syracuse, New York Laboratory, West Chester, Penn
E - Surface Water & Sediment Investigation: Sampling Analyses	O'Brien & Gere Engineers, Inc. O'Brien & Gere Laboratories, Inc. Roy F. Weston, Inc. Rocky Mountain Environmental Testing & Certification (ETC)	On-Site Laboratory, Syracuse, New York Laboratory, West Chester, Penn Denver, Colorado Laboratory, Edison, New York
F - Biota: Sampling Analyses	O'Brien & Gere Engineers, Inc. O'Brien & Gere Engineers, Inc.	On-Site Laboratory, Syracuse, New York
<u>Task 4</u> - Preliminary Remedial Technologies	O'Brien & Gere Engineers, Inc.	Main Office, Syracuse, New York
<u>Task 5</u> - Site Investigations Analysis	O'Brien & Gere Engineers, Inc.	Main Office, Syracuse, New York
<u>Task 6</u> - Final Report	O'Brien & Gere Engineers, Inc.	Main Office, Syracuse, New York
<u>Task 7</u> - Community Relations	Fish and Wildlife Service	On-Site
<u>Task 8</u> - Additional Requirements	O'Brien & Gere Engineers, Inc.	Main Office, Syracuse, New York

TABLE 8A
ANALYTICAL RESPONSIBILITIES

<u>Parameters</u>		Roy F. Weston Inc.	Envir. Testing and Certif.	OB&G Labs Inc.	Rocky Mt. Labs
1.	Purgeable Priority Pollutants		X		
2.	Acid Extract Priority Pollutants		X		
3.	Base/Neutral Extract Priority Pollutants		X		
4.	Pesticide/PCB Priority Pollutants		X		
5.	PCB's			X	
6.	Metals			X	X
7.	Explosives Residues by HPLC	X			
8.	PCOD/PCDF		X		
9.	Nitrogen Series		X		
10.	Drinking Water STD's			X	
11.	Total Phosphorus		X		
12.	Other			X	
	PCB's (ppt level)				
	Nitrosamines (ppt level)				

*Are these included
in Phase II?*

- 1 - Roy F. Weston, Inc., West Chester, Pennsylvania
- 2 - Environmental Testing Certification, Edison, New Jersey
- 3 - O'Brien & Gere Labs, Inc., Syracuse, New York
- 4 - Rocky Mountain Labs, Denver, Colorado

FIGURE 3

PROJECT ORGANIZATION

REMEDIAL INVESTIGATION/FEASIBILITY STUDY

CRAB ORCHARD NATIONAL WILDLIFE REFUGE

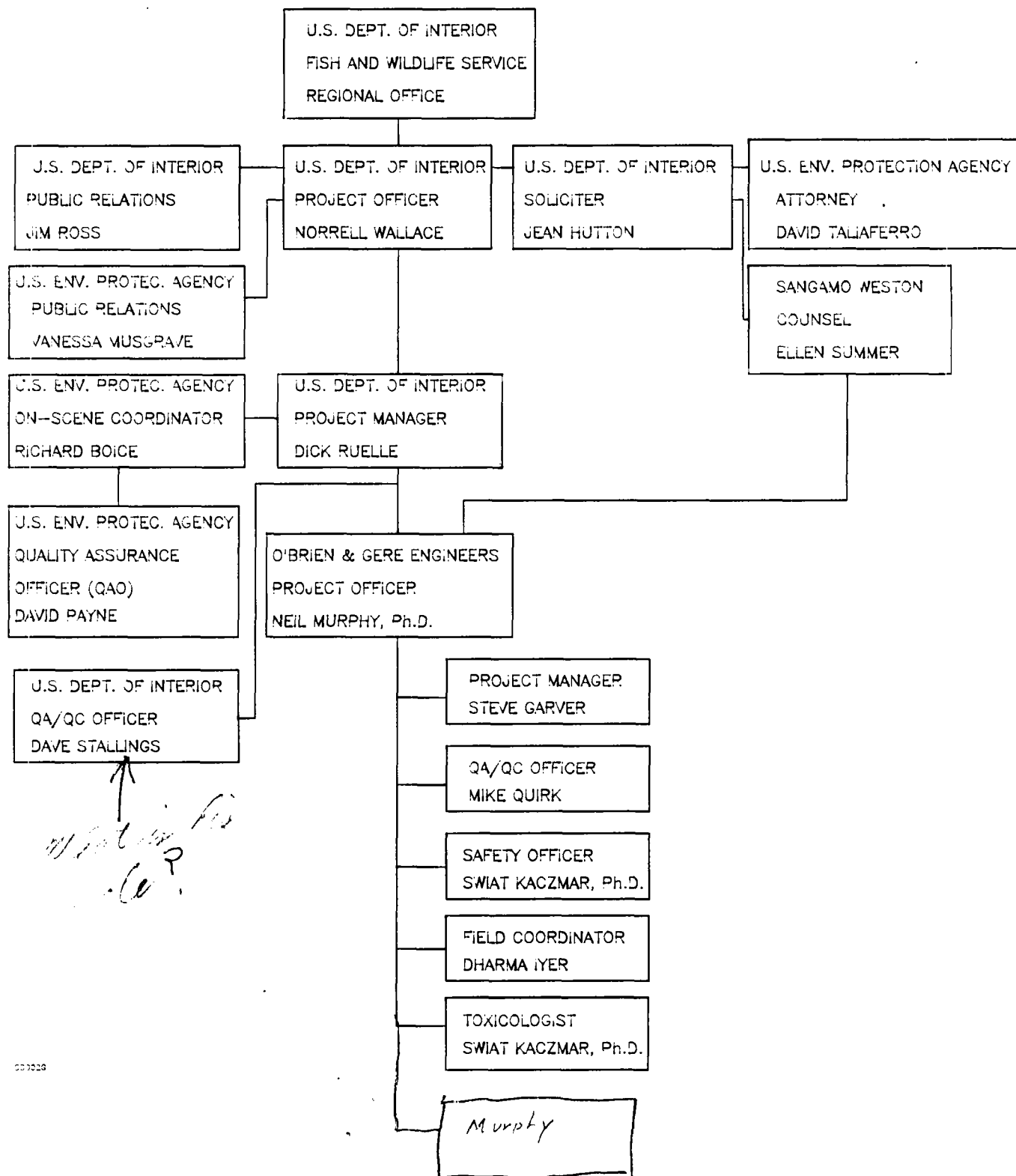
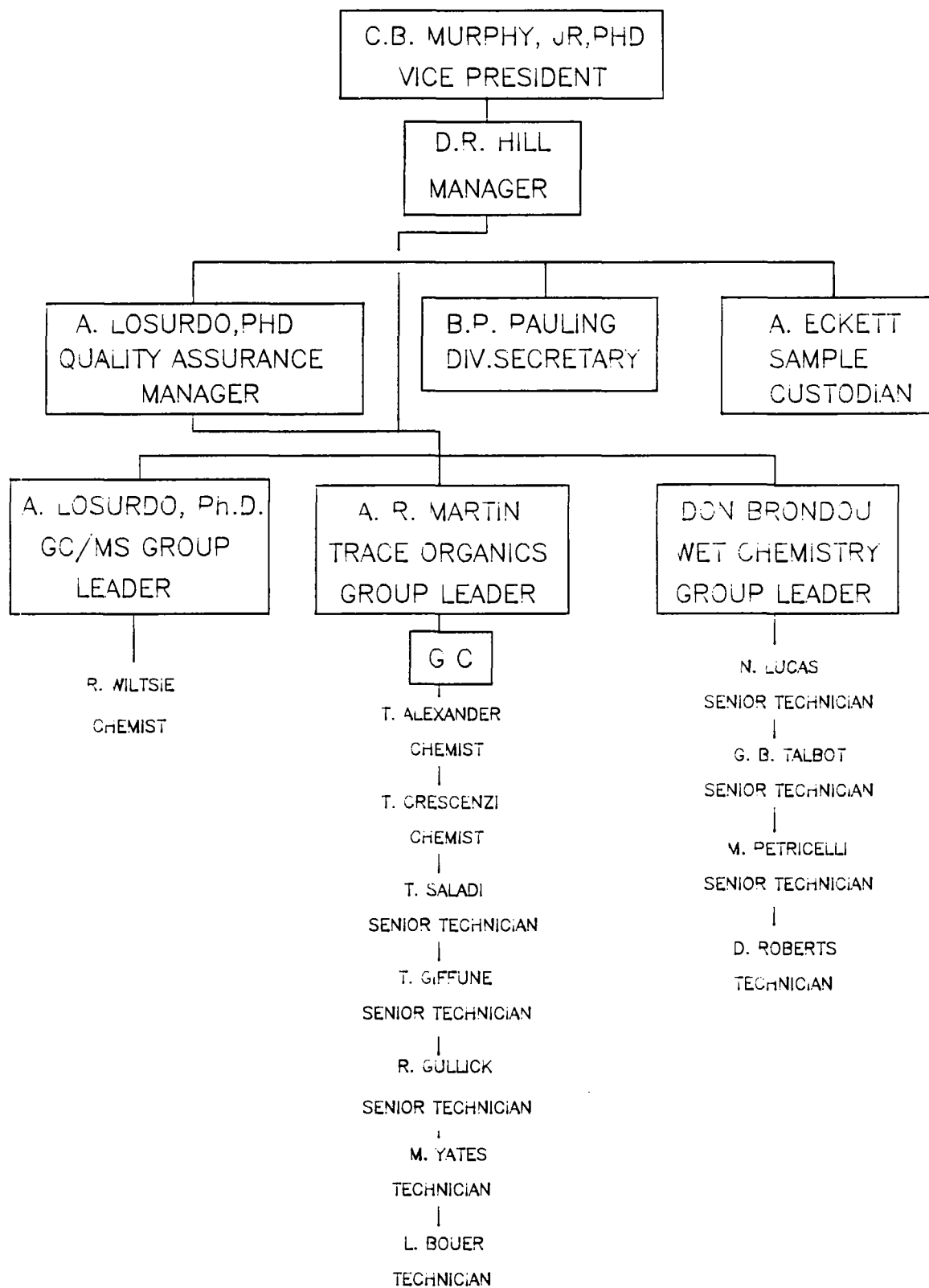


FIGURE 4

LABORATORY ORGANIZATION CHART



items marked are not
in CLP

Table 10, Page 1 of 19
ANALYTICAL METHOD: WATER
VOLATILES

56 WA 85-J664

WA 85-J680

CHEMICAL COMPOUND	METHOD	DETECTION LIMIT	AUDIT	FREQUENCY	CONTROL LIMITS
	(CLP)	ppb			
1,1,1-trichloroethane	WA 85-177	10	SEE BELOW	SEE BELOW	SEE BELOW
1,1,2,2-tetrachloroethane	WA 85-177	10	"	"	"
1,1,2-trichloroethane	WA 85-177	10	"	"	"
1,1-dichloroethane	WA 85-177	10	"	"	"
1,1-dichloroethene	WA 85-177	10	"	"	"
1,2-dichloropropane	WA 85-177	10	"	"	"
2-bromo-1-chloropropane	WA 85-177	10	"	"	"
2-butanone	WA 85-177	10	"	"	"
2-chloroethylvinyl ether	WA 85-177	10	"	"	"
2-hexanone	WA 85-177	10	"	"	"
4-methyl-2-pentanone	WA 85-177	10	"	"	"
acetone	WA 85-177	10	"	"	"
benzene	WA 85-177	10	"	"	"
bromochloromethane	WA 85-177	10	"	"	"
bromodichloromethane	WA 85-177	10	"	"	"
bromoform	WA 85-177	10	"	"	"
bromomethane	WA 85-177	10	"	"	"
c-1,3-dichloropropene	WA 85-177	10	"	"	"
carbon tetrachloride	WA 85-177	10	"	"	"
chlorobenzene	WA 85-177	10	"	"	"
chloroethane	WA 85-177	10	"	"	"
chloroform	WA 85-177	10	"	"	"
chloromethane	WA 85-177	10	"	"	"
dibromochloromethane	WA 85-177	10	"	"	"
dichlorodifluoromethane	WA 85-177	10	"	"	"
ethyl benzene	WA 85-177	10	"	"	"
methylene chloride	WA 85-177	10	"	"	"
t-1,1-trichloroethene	WA 85-177	10	"	"	"
t-1,3-dichloropropene	WA 85-177	10	"	"	"
tetrachloroethene	WA 85-177	10	"	"	"
toluene	WA 85-177	10	"	"	"
total xylenes	WA 85-177	10	"	"	"
trichloroethene	WA 85-177	10	"	"	"
trichlorofluoromethane	WA 85-177	10	"	"	"
vinyl acetate	WA 85-177	10	"	"	"
vinyl chloride	WA 85-177	10	"	"	"

CLP parameters
not listed
carbon disulfide
trans 1,2 dichloro-
ethene
1,2 dichloroethene
1,2 dichloroethane
trans 1,3 dichloropropene
~~trans 1,3 dichloropropene~~
styrene

AUDIT	FREQUENCY	CONTROL LIMITS
Reagent Blank	1 per case or 1 in 20 of similar concentration /matrix.	Less than 5x CRDL for solvents, less than CRDL for all others
Surrogate Spike	All samples and blank (including MS/MSD).	Recovery limits within those of Table 4.2, Exhibit E WA 85-J177 (revised 1/85).
MS/MSD	1 per case or 1 in 20 of similar concentration /matrix.	Recovery limits within those of Table 5.2, Exhibit E WA 85-J177 (revised 1/85).
Calibration Continuing	Each 12 hours	Minimum RF 0.003; must be less than 25% difference for any check compound.
Method/Field Blank	1 in 20-provided by sampling crew	Same as reagent blank
Replicate	1 in 20-provided by sampling crew	±20% PRE waters
MS Tuning	One per day.	BFB key ions and abundance criteria must be met for all 9 ions.
Calibration Verification	Once	Five concentrations - linear range volatiles 0-500 mg.

make separate
table for separate
parameter groups.

See Hong's comments in red

Table 10, Page 2 of 19
ANALYTICAL METHOD: WATER
BASE/NEUTRALS

correct parameters
8/7/88

CHEMICAL COMPOUND	METHOD	DETECTION LIMIT	AUDIT	FREQUENCY	CONTROL LIMITS
	(CLP)	ppb			
1,2,4-trichlorobenzene	WA 85-177	10	SEE BELOW	SEE BELOW	SEE BELOW
1,2-dichlorobenzene	WA 85-177	10	"	"	"
1,2-diphenylhydrazine	WA 85-177	10	"	"	"
1,3-dichlorobenzene	WA 85-177	10	"	"	"
1,4-dichlorobenzene	WA 85-177	10	"	"	"
2,4-dinitrotoluene	WA 85-177	10	"	"	"
2,6-dinitrotoluene	WA 85-177	10	"	"	"
2-chloronaphthalene	WA 85-177	10	"	"	"
3,3-dichlorobenzidine	WA 85-177	10	"	"	"
4-bromophenyl phenyl ether	WA 85-177	10	"	"	"
4-chlorophenyl phenyl ether	WA 85-177	10	"	"	"
acenaphthalene	WA 85-177	10	"	"	"
acenaphthene	WA 85-177	10	"	"	"
anthracene	WA 85-177	10	"	"	"
benzo(a)anthracene	WA 85-177	10	"	"	"
benzo(a)pyrene	WA 85-177	10	"	"	"
benzo(b)fluoranthene	WA 85-177	10	"	"	"
benzo(g,h,i)perylene	WA 85-177	10	"	"	"
benzo(k)fluoranthene	WA 85-177	10	"	"	"
bis(2-chloroethoxy)methane	WA 85-177	10	"	"	"
bis(2-chloroethyl) ether	WA 85-177	10	"	"	"
bis(2-chloroisopropyl) ether	WA 85-177	10	"	"	"
bis(2-ethylhexyl)phthalate	WA 85-177	10	"	"	"
butyl benzyl phthalate	WA 85-177	10	"	"	"
chrysene	WA 85-177	10	"	"	"
di-n-butylphthalate	WA 85-177	10	"	"	"
di-n-octyl phthalate	WA 85-177	10	"	"	"
dibenzo(a,h)anthracene	WA 85-177	10	"	"	"
diethyl phthalate	WA 85-177	10	"	"	"
dimethyl phthalate	WA 85-177	10	"	"	"
fluoranthene	WA 85-177	10	"	"	"
fluorene	WA 85-177	10	"	"	"
hexachlorobenzene	WA 85-177	10	"	"	"
hexachlorobutadiene	WA 85-177	10	"	"	"
hexachlorocyclopentadiene	WA 85-177	10	"	"	"
hexachloroethane	WA 85-177	10	"	"	"
indeno(1,2,3-c,d)pyrene	WA 85-177	10	"	"	"
isophorone	WA 85-177	10	"	"	"
N-nitrosodi-n-propylamine	WA 85-177	10	"	"	"
N-nitrosodimethylamine	WA 85-177	10	"	"	"
N-nitrosodiphenylamine	WA 85-177	10	"	"	"
naphthalene	WA 85-177	10	"	"	"
nitrobenzene	WA 85-177	10	"	"	"
phenanthrene	WA 85-177	10	"	"	"
pyrene	WA 85-177	10	"	"	"

AUDIT	FREQUENCY	CONTROL LIMITS
Reagent Blank	1 per case or 1 in 20 of similar concentration/matrix.	Less than 5x CRDL for solvents, less than CRDL for all others
Surrogate Spike	All samples and blank (including MS/MSD).	Recovery limits within those of Table 4.2, Exhibit E WA 85-J177.
MS/MSD	1 per case or 1 in 20 of similar concentration/matrix.	Recovery limits within those of Table 5.2, Exhibit E WA 85-J177.
Calibration Continuing	Each 12 hours	Minimum RF 0.05; must be less than 25% difference for any check compound.
Method/Field Blank	1 in 20-provided by sampling crew	Same as reagent blank
Replicate	1 in 20-provided by smpling crew	±20% PRE waters
MS Tuning	One per day.	DFTPP key ions & abundance criteria must be met for all 13 ions.
Calibration Verification	Once	Five concentrations - linear range Base/Neutrals 0-400 ng. Acids 0-1000 ng.

*Options allowed in method 2
option needs to be specified*

Table 10, Page 3 of 19
ANALYTICAL METHOD: WATER
PESTICIDES/PCBs

*Correct WA#
detection limits
& parameters*

CHEMICAL COMPOUND	METHOD 1	DETECTION LIMIT 1	METHOD 2	DETECTION LIMIT 2	AUDIT	FREQUENCY	CONTROL LIMITS
	(GC)	ppb	(CLP)	ppb			
4,4'-DDD			WA 85-177	10	SEE BELOW	SEE BELOW	SEE BELOW
4,4'-DDE			WA 85-177	10	"	"	"
4,4'-DDT			WA 85-177	10	"	"	"
aldrin			WA 85-177	10	"	"	"
Aroclor 1016	608	0.5	WA 85-177	10	"	"	"
Aroclor 1221	608	0.5	WA 85-177	10	"	"	"
Aroclor 1232	608	0.5	WA 85-177	10	"	"	"
Aroclor 1242	608	0.5	WA 85-177	10	"	"	"
Aroclor 1248	608	0.5	WA 85-177	10	"	"	"
Aroclor 1254	608	1.0	WA 85-177	10	"	"	"
Aroclor 1260	608	1.0	WA 85-177	10	"	"	"
chlordane			WA 85-177	10	"	"	"
dieldrin			WA 85-177	10	"	"	"
endosulfan I			WA 85-177	10	"	"	"
endosulfan II			WA 85-177	10	"	"	"
endosulfan sulfate			WA 85-177	10	"	"	"
endrin			WA 85-177	10	"	"	"
endrin aldehyde			WA 85-177	10	"	"	"
endrin ketone			WA 85-177	10	"	"	"
heptachlor			WA 85-177	10	"	"	"
heptachlor epoxide			WA 85-177	10	"	"	"
methoxychlor			WA 85-177	10	"	"	"
toxaphene			WA 85-177	10	"	"	"
α -BHC			WA 85-177	10	"	"	"
γ -BHC (lindane)			WA 85-177	10	"	"	"
δ -BHC			WA 85-177	10	"	"	"

*Which method
will be used?*

AUDIT	FREQUENCY	CONTROL LIMITS
Retention Time Windows	Once per 24 hours	4,4'-DDT must have retention time greater than or equal to 12 minutes on packed column, less than 2% shift on packed and .3% for capillary column.
Evaluation Mixtures A, B, & C	Once per 72 hours.	% RSD for aldrin, endrin & dibutylchloroendate must be less than or equal to 10%.
Column Breakthrough	Once per 72 hours.	Must not exceed 20% - if greater remedial action is required.
Standard Mix	Once per 72 hours then intermittently throughout analysis	Calculated factors must not exceed 15% difference for the quantitation run nor 20% difference for confirmation run during 12-hr period. Deviation greater than or equal to 15% requires reanalysis.
Confirmation Analysis	Once per 72 hours.	Separation should be greater than or equal to 25% resolution between peaks.
Reagent Blank	1 per case or 1 in 20 of similar concentration/matrix.	Less than 5x CRDL for solvents, less than CRDL for all others.
Surrogate Spike	All samples and blank (including MS/MSD).	Recovery limits within those of Table 4.2, Exhibit E WA 85-J177.
MS/MSD	1 per case or 1 in 20 of similar concentration/matrix.	Must fall within limits of Table 5.2, Exhibit E WA 85-J177.

① Low level 955's.

Table 10, Page 4 of 19
ANALYTICAL METHOD: WATER
ACID EXTRACTABLES

*In CLP acid ext
are analyzed with
BIV's. & do not make a
separate
category.*

CHEMICAL COMPOUND	METHOD	DETECTION LIMIT	AUDIT	FREQUENCY	CONTROL LIMITS
	(CLP)	ppb			
2,4,6-trichlorophenol	WA 85-177	10	SEE BELOW	SEE BELOW	SEE BELOW
2,4-dichlorophenol	WA 85-177	10	"	"	"
2,4-dimethylphenol	WA 85-177	10	"	"	"
2,4-dinitrophenol	WA 85-177	50	"	"	"
2-chlorophenol	WA 85-177	10	"	"	"
2-fluorophenol	WA 85-177	10	"	"	"
2-methyl-4,6-dinitrophenol	WA 85-177	50	"	"	"
2-nitrophenol	WA 85-177	10	"	"	"
4-chloro-3-methylphenol	WA 85-177	10	"	"	"
4-nitrophenol	WA 85-177	50	"	"	"
pentachlorophenol	WA 85-177	50	"	"	"
pentafluorophenol	WA 85-177	50	"	"	"
phenol	WA 85-177	10	"	"	"

*Correct W/H#
dlt parameters*

AUDIT	FREQUENCY	CONTROL LIMITS
Reagent Blank	1 per case or 1 in 20 of similar concentration/matrix.	Less than 5x CRDL for solvents, less than CRDL for all others
Surrogate Spike	All samples and blank (including MS/MSD).	Recovery limits within those of Table 4.2, Exhibit E WA 85-J177.
MS/MSD	1 per case or 1 in 20 of similar concentration/matrix.	Recovery limits within those of Table 5.2, Exhibit E WA 85-J177.
Calibration Continuing	Each 12 hours	Minimum RF 0.05; must be less than 25% difference for any check compound.
Method/Field Blank	1 in 20-provided by sampling crew	Same as reagent blank
Replicate	1 in 20-provided by sampling crew	±20% PRE waters
MS Tuning	One per day.	DFTPP key ions & abundance criteria must be met for all 13 ions.
Calibration Verification	Once	Five concentrations - linear range Base/Neutrals 0-400 ng. Acids 0-1000 ng.

*Matrix spikes and matrix spike
duplicates are not identified.*

*See found
this.*

Table 10, Page 5 of 19
ANALYTICAL METHOD: WATER
METALS

CRL uses furnace.

CHEMICAL COMPOUND	METHOD	DETECTION LIMIT	AUDIT	FREQUENCY	CONTROL LIMITS
	*	ppb			
aluminum	202.1	100	SEE BELOW	SEE BELOW	SEE BELOW
antimony	204.1	200	"	"	"
arsenic	206.2	1	"	"	"
barium	208.1	100	"	"	"
beryllium	210.1	5	"	"	"
cadmium	213.2	0.1	"	"	"
calcium	215.1	10	"	"	"
chromium	218.2	1	"	"	"
cobalt	219.1	50	"	"	"
copper	220.2	20	"	"	"
iron	236.1	30	"	"	"
lead	239.2	1	"	"	"
magnesium	242.1	10	"	"	"
manganese	243.1	10	"	"	"
mercury (cold vapor)	245.1	0.2	"	"	"
molybdenum	246.1	100	"	"	"
nickel	249.1	40	"	"	"
potassium	258.1	10	"	"	"
selenium	270.2	2	"	"	"
silver	272.1	10	"	"	"
sodium	273.1	10	"	"	"
tin	282.1	800	"	"	"
titanium	283.1	400	"	"	"
vanadium	286.1	200	"	"	"
zinc	289.1	5	"	"	"

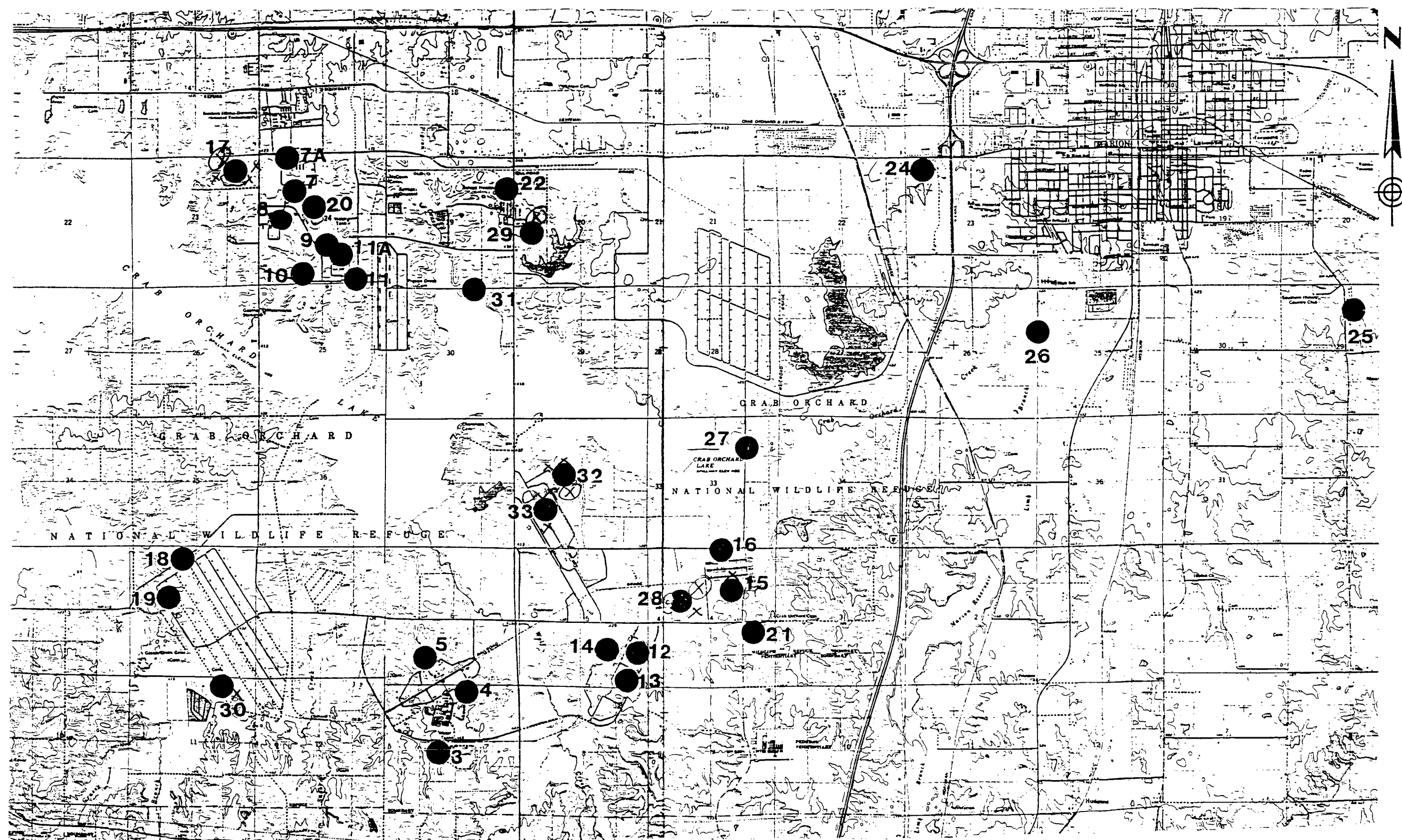
Pharma will hook on.

- 2 diff bottles

* - Methods reference: AA by direct aspiration (methods xxx.1) or furnace (methods xxx.2), EPA-600/4-79-220 "Method for Chemical Analysis of Water and Waste Water."

AUDIT	FREQUENCY	CONTROL LIMITS
Calibration	Calibrated daily and each time instrument is set up; verify at at a frequency of 10% or every 2 hr, whichever is greater.	Within $\pm 10\%$ of true value for all except tin and mercury ($\pm 20\%$ of true value).
Verification		
Calibration Blank	During calibration at a frequency of 10% during run and at end of run.	No more than CRDL.
Preparation Blank	1 per batch of samples digested or 1 in 20 whichever is greater	No more than CRDL.
Interference Check Sample	at beginning and end of or twice per 8-hr working shift, whichever is greater.	$\pm 20\%$ of mean value (established by running samples at least 5 times repetitively).
Spiked Sample Analysis	1 per group of similar concentration and matrix, 1 per case of samples, or 1 in 20, whichever is greater.	Within $\pm 25\%$ recovery
Duplicate Sample Analysis	Same as spiked sample analysis.	$\pm 20\%$ RPD for values 5X CRDL or more \pm CRDL for samples less than 5X CRDL.
Lab Control Sample (aqueous)	1 for each procedure for each case of samples received; 1 in 20 or 1 per batch digested, whichever is greater.	Within 80-120% recovery
Spike Sample	each analysis	In accordance with limits shown in Section 7, Exhibit E, SOW no. 784 (July 1984)

FIGURE 1



CRAB ORCHARD NATIONAL WILDLIFE REFUGE

LOCATIONS OF SAMPLING SITES

Scale: 1" = 4000'

Table 10, Page 5A of 19
ANALYTICAL METHOD: WATER
METALS

Dissolved Metals: Those constituents (metals) which will pass through a 0.45 μ membrane filter.

Field Filtration Protocol:

An aliquot of sample will be passed through a 0.45 μ membrane filter by one of the following methods:

- 1) Plastic syringe equipped with a filter holder (Swinnex Filter Holder).
- 2) Hand vacuum pump and a 500 ml side arm, glass filtration flask.
- 3) Bench top (electric) filtration system.

*Standards and samples will be matrix-matched to the concentration of the mineral acid.

*Calibration curves, continuing calibration and corrective measures records will be documented.

*One medium range internal synthetic standard will be analyzed to verify calibration and will be within $\pm 10\%$ of true value

*Furnace work will require duplicate analysis of each sample to verify recovery of spiked material. If recoveries are within $\pm 10\%$, methods of addition will not be required. If outside this criterion, methods of standard addition will be required.

*For chromium analysis, a nitrous oxide flame will be used.

Table 10, Page 6 of 19
ANALYTICAL METHOD: WATER
WET CHEMISTRY

should vs. method able to reach 5-10 ppt.

nb 335.3
335.2
screening method

CHEMICAL COMPOUND	METHOD	DETECTION LIMIT	AUDIT	FREQUENCY	CONTROL LIMITS
	*	ppb			
cyanide	335.2	50	"	"	"
percent solids	160.3	0.1 %	"	"	"
pH	150.1	0.1 std units	"	"	"
total phosphorus	365.4	10	"	"	"
total suspended solids	209.c**	1000			

* Methods Reference: EPA-600/4-79-020 "Methods for Chemical Analysis of Water and Waste Waters"

** Standard Methods for the Evaluation of Water and Wastewater. 16th Ed. 1985.

AUDIT	FREQUENCY	CONTROL LIMITS
Calibration	calibrated daily and each time instrument is set up; verify at a frequency of 10% or every 2 whichever is greater.	Within $\pm 10\%$ of true value.
Verification		
Calibration Blank	during calibration, at a frequency of 10% during run, and at end of run.	No more than CRDL
Preparation Blank	1 per batch of samples or 1 in 20, whichever is greater.	No more than CRDL
Interference Check Sample	At beginning and end of each run or twice per 8-hr working shift.	$\pm 20\%$ of mean value (established by running sample at least 5 times repetitively); check sample to be prepared in consultation with EPA.
Duplicate Sample Analysis	1 per case of samples or 1 in 20, whichever is greater.	$\pm 20\%$ RPD for values 5X CRDL or more; \pm CRDL for samples less than 5X CRDL.
Spiked Sample Analysis	1 per group of similar concentration, 1 per case of samples, or 1 in 20; 1 at end of run for nitrate and nitrite.	within $\pm 25\%$ recovery

Additional Parameters

ammonia

nitrate

nitrite

PCB's (ppt level)

nitrosamines (ppt level)

the rest of C.

Table 10, Page 7 of 19
ANALYTICAL METHOD: WATER
EXPLOSIVES

CHEMICAL COMPOUND	METHOD	DETECTION LIMIT	AUDIT	FREQUENCY	CONTROL LIMITS
1,3 DNB	SEE NOTE 6	ppb 0.5			
1,3,5 TNB	SEE NOTE 6	0.5			
2,4 DNT	SEE NOTE 6	0.5			
2,4,6 TNT	SEE NOTE 6	0.7			
2,6 DNT	SEE NOTE 6	0.5			
HMX	SEE NOTE 6	2.0			
NB	SEE NOTE 6	0.4			
RDX	SEE NOTE 6	1.2			
tetryl	SEE NOTE 6	0.6			

NOTE 6 USATHAWA Method 2C Cyclotrimethylenetrinitramine (RDX) samples, 12/8/80.

Table 10, Page 8 of 19
ANALYTICAL METHOD: SOIL/SEDIMENT
VOLATILES

CHEMICAL COMPOUND	METHOD	DETECTION LIMIT	AUDIT	FREQUENCY	CONTROL LIMITS
	(CLP)	ppb			
1,1,1-trichloroethane	WA 85-177	10	SEE BELOW	SEE BELOW	SEE BELOW
1,1,2,2-tetrachloroethane	WA 85-177	10	"	"	"
1,1,2-trichloroethane	WA 85-177	10	"	"	"
1,1-dichloroethane	WA 85-177	10	"	"	"
1,1-dichloroethene	WA 85-177	10	"	"	"
1,2-dichloropropane	WA 85-177	10	"	"	"
2-bromo-1-chloropropane	WA 85-177	10	"	"	"
2-butanone	WA 85-177	10	"	"	"
2-chloroethylvinyl ether	WA 85-177	10	"	"	"
2-hexanone	WA 85-177	10	"	"	"
4-methyl-2-pentanone	WA 85-177	10	"	"	"
acetone	WA 85-177	10	"	"	"
benzene	WA 85-177	10	"	"	"
bromochloromethane	WA 85-177	10	"	"	"
bromodichloromethane	WA 85-177	10	"	"	"
bromoform	WA 85-177	10	"	"	"
bromomethane	WA 85-177	10	"	"	"
c-1,3-dichloropropene	WA 85-177	10	"	"	"
carbon tetrachloride	WA 85-177	10	"	"	"
chlorobenzene	WA 85-177	10	"	"	"
chloroethane	WA 85-177	10	"	"	"
chloroform	WA 85-177	10	"	"	"
chloromethane	WA 85-177	10	"	"	"
dibromochloromethane	WA 85-177	10	"	"	"
dichlorodifluoromethane	WA 85-177	10	"	"	"
ethyl benzene	WA 85-177	10	"	"	"
methylene chloride	WA 85-177	10	"	"	"
t-1,1-trichloroethene	WA 85-177	10	"	"	"
t-1,3-dichloropropene	WA 85-177	10	"	"	"
tetrachloroethene	WA 85-177	10	"	"	"
toluene	WA 85-177	10	"	"	"
total xylenes	WA 85-177	10	"	"	"
trichloroethene	WA 85-177	10	"	"	"
trichlorofluoromethane	WA 85-177	10	"	"	"
vinyl	WA 85-177	10	"	"	"
vinyl chloride	WA 85-177	10	"	"	"

AUDIT	FREQUENCY	CONTROL LIMITS
Reagent Blank	1 per case or 1 in 20 of similar concentration /matrix.	Less than 5x CRDL for solvents, less than CRDL for all others
Surrogate Spike	All samples and blank (including MS/MSD).	Recovery limits within those of Table 4.2, Exhibit E WA 85-J177 (revised 1/85).
MS/MSD	1 per case or 1 in 20 of similar concentration/matrix.	Recovery limits within those of Table 5.2, Exhibit E WA 85-J177 (revised 1/85).
Calibration Continuing	Each 12 hours	Minimum RF 0.003; must be less than 25% difference for any check compound.
Method/Field Blank	1 in 20-provided by sampling crew	Same as reagent blank
Replicate	1 in 20-provided by smping crew	±50% PRE soils - <i>at ± 30% to be wild check.</i>
MS Tuning	One per day.	BFB key ions and abundance criteria must be met for all 9 ions.
Calibration Verification	Once	Five concentrations - linear range volatiles 0-500 mg.

Table 10, Page 9 of 19
ANALYTICAL METHOD: SOIL/SEDIMENT
BASE/NEUTRALS

CHEMICAL COMPOUND	METHOD	DETECTION LIMIT	AUDIT	FREQUENCY	CONTROL LIMITS
	(CLP)	ppb			
1,2,4-trichlorobenzene	WA 85-177	330	SEE BELOW	SEE BELOW	SEE BELOW
1,2-dichlorobenzene	WA 85-177	330	"	"	"
1,2-diphenylhydrazine	WA 85-177	330	"	"	"
1,3-dichlorobenzene	WA 85-177	330	"	"	"
1,4-dichlorobenzene	WA 85-177	330	"	"	"
2,4-dinitrotoluene	WA 85-177	330	"	"	"
2,6-dinitrotoluene	WA 85-177	330	"	"	"
2-chloronaphthalene	WA 85-177	330	"	"	"
3,3-dichlorobenzidine	WA 85-177	330	"	"	"
4-bromophenyl phenyl ether	WA 85-177	330	"	"	"
4-chlorophenyl phenyl ether	WA 85-177	330	"	"	"
acenaphthalene	WA 85-177	330	"	"	"
acenaphthene	WA 85-177	330	"	"	"
anthracene	WA 85-177	330	"	"	"
benzidine	WA 85-177	330	"	"	"
benzo(a)anthracene	WA 85-177	330	"	"	"
benzo(a)pyrene	WA 85-177	330	"	"	"
benzo(b)fluoranthene	WA 85-177	330	"	"	"
benzo(g,h,i)perylene	WA 85-177	330	"	"	"
benzo(k)fluoranthene	WA 85-177	330	"	"	"
bis(2-chloroethoxy)methane	WA 85-177	330	"	"	"
bis(2-chloroethyl) ether	WA 85-177	330	"	"	"
bis(2-chloroisopropyl) ether	WA 85-177	330	"	"	"
bis(2-ethylhexyl)phthalate	WA 85-177	330	"	"	"
butyl benzyl phthalate	WA 85-177	330	"	"	"
chrysene	WA 85-177	330	"	"	"
di-n-butylphthalate	WA 85-177	330	"	"	"
di-n-octyl phthalate	WA 85-177	330	"	"	"
dibenzo(a,h)anthracene	WA 85-177	330	"	"	"
diethyl phthalate	WA 85-177	330	"	"	"
dimethyl phthalate	WA 85-177	330	"	"	"
fluoranthene	WA 85-177	330	"	"	"
fluorene	WA 85-177	330	"	"	"
hexachlorobenzene	WA 85-177	330	"	"	"
hexachlorobutadiene	WA 85-177	330	"	"	"
hexachlorocyclopentadiene	WA 85-177	330	"	"	"
hexachloroethane	WA 85-177	330	"	"	"
indeno(1,2,3-c,d)pyrene	WA 85-177	330	"	"	"
isophorone	WA 85-177	330	"	"	"
N-nitrosodi-n-propylamine *	WA 85-177	330	"	"	"
N-nitrosodimethylamine *	WA 85-177	330	"	"	"
N-nitrosodiphenylamine *	WA 85-177	330	"	"	"
naphthalene	WA 85-177	330	"	"	"
nitrobenzene	WA 85-177	330	"	"	"
phenanthrene	WA 85-177	330	"	"	"
pyrene	WA 85-177	330	"	"	"
AUDIT	FREQUENCY	CONTROL LIMITS			
Reagent Blank	1 per case or 1 in 20 of similar concentration/matrix.	Less than 5x CRDL for solvents, less than CRDL for all others			
Surrogate Spike	All samples and blank (including MS/MSD).	Recovery limits within those of Table 4.2, Exhibit E WA 85-J177.			
MS/MSD	1 per case or 1 in 20 of similar concentration/matrix.	Recovery limits within those of Table 5.2, Exhibit E WA 85-J177.			
Calibration Continuing	Each 12 hours	Minimum RF 0.05; must be less than 25% difference for any check compound.			
Method/Field Blank	1 in 20-provided by sampling crew	Same as reagent blank			
Replicate	1 in 20-provided by sampling crew	±50% PRE soils			
MS Tuning	One per day.	DFTPP key ions & abundance criteria must be met for all 13 ions.			
Calibration Verification	Once	Five concentrations - linear range Base/Neutrals 0-400 ng. Acids 0-1000 ng.			

* Procedures being developed in conjunction with EPA Region V to obtain detection levels of 150-800 ppt.

Table 10, Page 10 of 19
ANALYTICAL METHOD: SOIL/SEDIMENT
PESTICIDES/PCBs

CHEMICAL COMPOUND	METHOD 1	DETECTION LIMIT 1	METHOD 2	DETECTION LIMIT 2	AUDIT	FREQUENCY	CONTROL LIMITS
	(GC)	ppb	(CLP)	ppb			
4,4'-DDD			WA 85-177	16	SEE BELOW	SEE BELOW	SEE BELOW
4,4'-DDE			WA 85-177	16	"	"	"
4,4'-DDT			WA 85-177	16	"	"	"
aldrin			WA 85-177	8	"	"	"
Aroclor 1016	608 *	17	WA 85-177	80	"	"	"
Aroclor 1221	608 *	17	WA 85-177	80	"	"	"
Aroclor 1232	608 *	17	WA 85-177	80	"	"	"
Aroclor 1242	608 *	17	WA 85-177	80	"	"	"
Aroclor 1248	608 *	17	WA 85-177	80	"	"	"
Aroclor 1254	608 *	33	WA 85-177	160	"	"	"
Aroclor 1260	608 *	33	WA 85-177	160	"	"	"
chlordane			WA 85-177	80	"	"	"
dieldrin			WA 85-177	16	"	"	"
endosulfan I			WA 85-177	8	"	"	"
endosulfan II			WA 85-177	16	"	"	"
endosulfan sulfate			WA 85-177	16	"	"	"
endrin			WA 85-177	16	"	"	"
endrin aldehyde			WA 85-177	16	"	"	"
endrin ketone			WA 85-177	16	"	"	"
heptachlor			WA 85-177	8	"	"	"
heptachlor epoxide			WA 85-177	8	"	"	"
methoxychlor			WA 85-177	80	"	"	"
toxaphene			WA 85-177	160	"	"	"
β -BHC			WA 85-177	8	"	"	"
γ -BHC (lindane)			WA 85-177	8	"	"	"
α -BHC			WA 85-177	8	"	"	"

*Which method
will be used?*

AUDIT	FREQUENCY	CONTROL LIMITS
Retention Time Windows	Once per 24 hours	4,4'-DDT must have retention time greater than or equal to 12 minutes on packed column, less than 2% shift on packed and .3% for capillary column.
Evaluation Mixtures A, B, & C	Once per 72 hours.	% RSD for aldrin, endrin & dibutylchloroendate must be less than or equal to 10%.
Column Breakthrough	Once per 72 hours.	Must not exceed 20% - if greater remedial action is required.
Standard Mix	Once per 72 hours then intermittently throughout analysis	Calculated factors must not exceed 15% difference for the quantitation run nor 20% difference for confirmation run during 12-hr period. Deviation greater than or equal to 15% requires reanalysis.
Confirmation Analysis	Once per 72 hours.	Separation should be greater than or equal to 25% resolution between peaks.
Reagent Blank	1 per case or 1 in 20 of similar concentration/matrix.	Less than 5x CRDL for solvents, less than CRDL for all others.
Surrogate Spike	All samples and blank (including MS/MSD).	Recovery limits within those of Table 4.2, Exhibit E WA 85-J177.
MS/MSD	1 per case or 1 in 20 of similar concentration/matrix.	Must fall within limits of Table 5.2, Exhibit E WA 85-J177.

* A detection level of 1.0 ppm will be used for Area 9 Building Complex.

How?

Table 10, Page 11 of 19
ANALYTICAL METHOD: SOIL/SEDIMENT
ACID EXTRACTABLES

CHEMICAL COMPOUND	METHOD	DETECTION LIMIT	AUDIT	FREQUENCY	CONTROL LIMITS
	(CLP)	ppb			
2,4,6-trichlorophenol	WA 85-177	330	SEE BELOW	SEE BELOW	SEE BELOW
2,4-dichlorophenol	WA 85-177	330	"	"	"
2,4-dimethylphenol	WA 85-177	330	"	"	"
2,4-dinitrophenol	WA 85-177	1600	"	"	"
2-chlorophenol	WA 85-177	330	"	"	"
2-fluorophenol	WA 85-177	330	"	"	"
2-methyl-4,6-dinitrophenol	WA 85-177	1600	"	"	"
2-nitrophenol	WA 85-177	330	"	"	"
4-chloro-3-methylphenol	WA 85-177	330	"	"	"
4-nitrophenol	WA 85-177	1600	"	"	"
pentachlorophenol	WA 85-177	1600	"	"	"
pentafluorophenol	WA 85-177	1600	"	"	"
phenol	WA 85-177	330	"	"	"

AUDIT	FREQUENCY	CONTROL LIMITS
Reagent Blank	1 per case or 1 in 20 of similar concentration/matrix.	Less than 5x CRDL for solvents, less than CRDL for all others
Surrogate Spike	All samples and blank (including MS/MSD).	Recovery limits within those of Table 4.2, Exhibit E WA 85-J177.
MS/MSD	1 per case or 1 in 20 of similar concentration/matrix.	Recovery limits within those of Table 5.2, Exhibit E WA 85-J177.
Calibration Continuing	Each 12 hours	Minimum RF 0.05; must be less than 25% difference for any check compound.
Method/Field Blank	1 in 20-provided by sampling crew	Same as reagent blank
Replicate	1 in 20-provided by sampling crew	±50% PRE soils
MS Tuning	One per day.	DFTPP key ions & abundance criteria must be met for all 13 ions.
Calibration Verification	Once	Five concentrations - linear range Base/Neutrals 0-400 ng. Acids 0-1000 ng.

Table 10, Page 12 of 19
ANALYTICAL METHOD: SOIL/SEDIMENT
METALS

CHEMICAL COMPOUND	METHOD	DETECTION LIMIT	AUDIT	FREQUENCY	CONTROL LIMITS
	*	ppb			
aluminum	202.1	10000	SEE BELOW	SEE BELOW	SEE BELOW
antimony	204.1	20000	"	"	"
arsenic	206.2	100	"	"	"
barium	208.1	10000	"	"	"
beryllium	210.1	500	"	"	"
cadmium	213.1	500	"	"	"
calcium	215.1	1000	"	"	"
chromium	218.1	5000	"	"	"
cobalt	219.1	5000	"	"	"
copper	220.1	2000	"	"	"
iron	236.1	3000	"	"	"
lead	239.1	10000 ← high	"	"	"
magnesium	242.1	1000	"	"	"
manganese	243.1	1000	"	"	"
mercury (cold vapor)	7471	200	"	"	"
molybdenum	246.1	10000	"	"	"
nickel	249.1	4000	"	"	"
potassium	258.1	1000	"	"	"
selenium	270.2	200	"	"	"
silver	272.1	1000	"	"	"
sodium	273.1	1000	"	"	"
tin	282.1	80000	"	"	"
titanium	283.1	40000	"	"	"
vanadium	286.1	20000	"	"	"
zinc	289.1	500	"	"	"

* Methods Reference: AA by direct aspiration (methods xxx.1) or furnace (Methods xxx.2),
EPA-600/4-79-020 "Method for Chemical Analysis of Water and Waste"
Soil/Sediment Digestion Procedure, Reference Test Methods for Evaluating Solid Waste,
EPA SW 846, Section 3050 (Revised 4/84).
Procedure - HCL final reflux for furnace, Sb, Sn
HCL final reflux for flame, Al, Sb, Ba, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg,
Ni, K, Ag, Na, Ti, Sn, V, Zn
HNO3 final reflux for furnace metals As, Be, Cd, Cr, Co, Cu, Fe,
Pb, Mn, Ni, Se, Ag, Ti, V, Zn

AUDIT	FREQUENCY	CONTROL LIMITS
Calibration Verification	Calibrated daily and each time instrument is set up; verify at at a frequency of 10% or every 2 hr, whichever is greater.	Within $\pm 10\%$ of true value for all except tin and mercury ($\pm 20\%$ of true value).
Calibration Blank	During calibration at a fre- quency of 10% during run and at end of run.	No more than CRDL.
Preparation Blank	1 per batch of samples digested or 1 in 20 whichever is greater	No more than CRDL.
Interference Check Sample	at beginning and end of or twice per 8-hr working shift, whichever is greater.	$\pm 20\%$ of mean value (established by running samples at least 5 times repetitively).
Spiked Sample Analysis	1 per group of similar concen- tration and matrix, 1 per case of samples, or 1 in 20, which- ever is greater.	Within $\pm 25\%$ recovery <i>see will check.</i>
Duplicate Sample Analysis	Same as spiked sample analysis.	$\pm 50\%$ RPD for values 5X CRDL or more \pm CRDL for samples less than 5X CRDL
Lab Control Sample (soils)	once a month for each of the procedures (applied) to solid sample analysis.	Within limits established by EPA.
Spike Sample	each analysis	In accordance with limits shown in Section 7, Exhibit E, SOW no. 784 (July 1984)

Table 10, Page 13 of 19
ANALYTICAL METHOD: SOIL/SEDIMENT
WET CHEMISTRY

CHEMICAL COMPOUND	METHOD	DETECTION LIMIT	AUDIT	FREQUENCY	CONTROL LIMITS
cyanide	335.2	ppb 2000	SEE NOTE 1	"	"
percent solids	160.3	0.1 %	"	"	"
pH	150.1	1 S.U.	SEE NOTE 1	"	"
total phosphorus	365.4	1000	SEE NOTE 2	"	"

* - Method Reference: EPA-600/4-79-020 "Methods for Chemical Analysis of Water and Waste"

NOTE 1 SLUDGE/SOIL/SEDIMENT Aliquot are extracted with distilled deionized water for 24 hours and the supernant is analyzed by the referenced aqueous procedure

NOTE 2 A portion of the SLUDGE/SOIL/SEDIMENT is subjected to the block digestion procedure the resultant digestate is analyzed by the referenced procedure.

NOTE 3 A SLUDGE/SOIL/SEDIMENT sample is extracted with ethyl acetate and the extract is pyrolyzed for TOX.

AUDIT	FREQUENCY	CONTROL LIMITS
Calibration Verification	calibrated daily and each time instrument is set up; verify at a frequency of 10% or every 2 whichever is greater.	Within $\pm 10\%$ of true value.
Calibration Blank	during calibration, at a frequency of 10% during run, and at end of run.	No more than CRDL
Preperation Blank	1 per batch of samples or 1 in 20, whichever is greater.	No more than CRDL
Interference Check Sample	At beginning and end of each run or twice per 8-hr working shift.	$\pm 20\%$ of mean value (established by running sample at least 5 times repetitively); check sample to be prepared in consultation with EPA.
Duplicate Sample Analysis	1 per case of samples or 1 in 20, whichever is greater.	$\pm 50\%$ RPD for values 5X CRDL or more; \pm CRDL for samples less than 5X CRDL.
Spiked Sample Analysis	1 per group of similar concentration, 1 per case of samples, or 1 in 20; 1 at end of run for nitrate and nitrite.	within $\pm 40\%$ recovery

Table 10, Page 14 of 19
ANALYTICAL METHOD: SOIL/SEDIMENT
DIOXINS/FURANS

CHEMICAL COMPOUND	METHOD	DETECTION LIMIT	AUDIT	FREQUENCY	CONTROL LIMITS
tetra-CDD	SEE NOTE 9	ppt 20			
tetra-CDF	SEE NOTE 9	20			
penta-CDD	SEE NOTE 9	20			
penta-CDF	SEE NOTE 9	20			
hexa-CDD	SEE NOTE 9	20			
hexa-CDF	SEE NOTE 9	20			
hepta-CDD	SEE NOTE 9	200			
hepta-CDF	SEE NOTE 9	200			
octa-CDD	SEE NOTE 9	200			
octa-CDF	SEE NOTE 9	200			

NOTE 9 Determination of Parts-per-Trillion levels of polychlorinated Dibenzofuran and dioxins in environmental samples, Smith L.M., Johnson J.C., Analytic Chemistry 1984, 56, 1830-1842, September 1984.



~~These are not included
in Phase II.~~

Table 10, Page 15 of 19
ANALYTICAL METHOD: SOIL/SEDIMENT
EXPLOSIVES

CHEMICAL COMPOUND	METHOD	DETECTION LIMIT	AUDIT	FREQUENCY	CONTROL LIMITS
1,3 DNB	SEE NOTE 6	ppb 500			
1,3,5 TNB	SEE NOTE 6	500			
2,4 DNT	SEE NOTE 6	500			
2,4,6 TNT	SEE NOTE 6	500			
2,6 DNT	SEE NOTE 6	500			
HMX	SEE NOTE 6	500			
NB	SEE NOTE 6	500			
RDX	SEE NOTE 6	500			
tetryl	SEE NOTE 6	500			

NOTE 6 USATHAWA Method 2C Cyclotrimethylenetrinitritamine (RDX) in soil
and sediment samples, 12/8/80.

Table 10, Page 16 of 19
ANALYTICAL METHOD: BIOTA
PESTICIDES/PCBs

CHEMICAL COMPOUND	METHOD	DETECTION LIMIT	AUDIT	FREQUENCY	CONTROL LIMITS
	GC/MS	ppb			
4,4'-DDD	SEE NOTE 12	50	SEE BELOW	SEE BELOW	SEE BELOW
4,4'-DDE	SEE NOTE 12	50	"	"	"
4,4'-DDT	SEE NOTE 12	50	"	"	"
aldrin	SEE NOTE 12	50	"	"	"
Aroclor 1016 *	SEE NOTE 12	50	"	"	"
Aroclor 1221 *	SEE NOTE 12	50	"	"	"
Aroclor 1232 *	SEE NOTE 12	50	"	"	"
Aroclor 1242 *	SEE NOTE 12	50	"	"	"
Aroclor 1248 *	SEE NOTE 12	50	"	"	"
Aroclor 1254 *	SEE NOTE 12	50	"	"	"
Aroclor 1260 *	SEE NOTE 12	50	"	"	"
chlordane	SEE NOTE 12	50	"	"	"
dieldrin	SEE NOTE 12	50	"	"	"
endosulfan I	SEE NOTE 12	50	"	"	"
endosulfan II	SEE NOTE 12	50	"	"	"
endosulfan sulfate	SEE NOTE 12	50	"	"	"
endrin	SEE NOTE 12	50	"	"	"
endrin aldehyde	SEE NOTE 12	50	"	"	"
endrin ketone	SEE NOTE 12	50	"	"	"
heptachlor	SEE NOTE 12	50	"	"	"
heptachlor epoxide	SEE NOTE 12	50	"	"	"
methoxychlor	SEE NOTE 12	50	"	"	"
toxaphene	SEE NOTE 12	50	"	"	"
β -BHC	SEE NOTE 12	50	"	"	"
γ -BHC (lindane)	SEE NOTE 12	50	"	"	"
α -BHC	SEE NOTE 12	50	"	"	"

*See 'em't
know what.*

NOTE 12 Sampling and Analysis Procedures for Surveying of Fish for Priority Pollutants USEPA June 1977.

AUDIT	FREQUENCY	CONTROL LIMITS
Retention Time Windows	Once per 24 hours	4,4'-DDT must have retention time greater than or equal to 12 minutes on packed column, less than 2% shift on packed and .3% for capillary column.
Evaluation Mixtures A, B, & C	Once per 72 hours.	% RSD for aldrin, endrin & dibutylchloroendate must be less than or equal to 10%.
Column Breakthrough	Once per 72 hours.	Must not exceed 20% - if greater remedial action is required.
Standard Mix	Once per 72 hours then intermittently throughout analysis	Calculated factors must not exceed 15% difference for the quantitation run nor 20% difference for confirmation run during 12-hr period. Deviation greater than or equal to 15% requires reanalysis.
Confirmation Analysis	Once per 72 hours.	Separation should be greater than or equal to 25% resolution between peaks.
Reagent Blank	1 per case or 1 in 20 of similar concentration/matrix.	Less than 5x CRDL for solvents, less than CRDL for all others.
Surrogate Spike	All samples and blank (including MS/MSD).	Recovery limits within those of Table 4.2, Exhibit E WA 85-J177.
MS/MSD	1 per case or 1 in 20 of similar concentration/matrix.	Must fall within limits of Table 5.2, Exhibit E WA 85-J177.

* Detection level may be increased to 0.1 ppm. (To be confirmed with EPA Region V.)

Table 10, Page 17 of 19
ANALYTICAL METHOD: BIOTA
METALS

CHEMICAL COMPOUND	METHOD	DETECTION LIMIT	AUDIT	FREQUENCY	CONTROL LIMITS
cadmium	SEE NOTE 12	ppb 10	SEE BELOW	SEE BELOW	SEE BELOW
lead	SEE NOTE 12	10000	"	"	"
mercury (cold vapor)	SEE NOTE 12	20	"	"	"

NOTE 12 Sampling and Analysis Procedures for Surveying of Fish for Priority Pollutants USEPA June 1977.

AUDIT	FREQUENCY	CONTROL LIMITS
Calibration Verification	Calibrated daily and each time instrument is set up; verify at a frequency of 10% or every 2 hr, whichever is greater.	Within $\pm 10\%$ of true value for all except tin and mercury ($\pm 20\%$ of true value).
Calibration Blank	During calibration at a frequency of 10% during run and at end of run.	No more than CRDL.
Preparation Blank	1 per batch of samples digested or 1 in 20 whichever is greater	No more than CRDL.
Interference Check Sample	at beginning and end of or twice per 8-hr working shift, whichever is greater.	$\pm 20\%$ of mean value (established by running samples at least 5 times repetitively).
Spiked Sample Analysis	1 per group of similar concentration and matrix, 1 per case of samples, or 1 in 20, whichever is greater.	Within $\pm 25\%$ recovery
Duplicate Sample Analysis	Same as spiked sample analysis.	$\pm 50\%$ RPD for values 5X CRDL or more \pm CRDL for samples less than 5X CRDL
Lab Control Sample (soils)	once a month for each of the procedures (applied) to solid sample analysis.	Within limits established by EPA.
Spike Sample	each analysis	In accordance with limits shown in Section 7, Exhibit E, SOW no. 784 (July 1984)

Table 10, Page 18 of 19
ANALYTICAL METHOD: BIOTA
LIPIDS

CHEMICAL COMPOUND	METHOD	DETECTION LIMIT	AUDIT	FREQUENCY	CONTROL LIMITS
lipids (oil & grease)	* 413-1	ppm 100**	SEE BELOW	SEE BELOW	SEE BELOW

* Methods reference: EPA-600/4-79-020, Methods for Chemical Analysis of Water and Wastewater.
** Based upon 50 grams of sample.

AUDIT	FREQUENCY	CONTROL LIMITS
Calibration Verification	calibrated daily and each time instrument is set up; verify at a frequency of 10% or every 2 whichever is greater.	Within $\pm 10\%$ of true value.
Calibration Blank	during calibration, at a fre- quency of 10% during run, and at end of run.	No more than CRDL
Preparation Blank	1 per batch of samples or 1 in 20, whichever is greater.	No more than CRDL
Interference Check Sample	At beginning and end of each run or twice per 8-hr work- ing shift.	$\pm 20\%$ of mean value (established by running sample at least 5 times repetitively); check sample to be prepared in consultation with EPA.
Duplicate Sample Analysis	1 per case of samples or 1 in 20, whichever is greater.	$\pm 50\%$ RPD for values 5X CRDL or more; \pm CRDL for samples less than 5X CRDL.
Spiked Sample Analysis	1 per group of similar concen- tration, 1 per case of samples, or 1 in 20; 1 at end of run for nitrate and nitrite.	within $\pm 40\%$ recovery

ABBREVIATIONS USED IN TABLE 10

CRDL	- CONTRACT REQUIRED DETECTION LIMITS
RF	- RESPONSE FACTOR
PRE	- PERCENT RELATIVE ERROR
MS/MSD	- MATRIX SPIKE/MATRIX SPIKE DUPLICATE
RPD	- RELATIVE PERCENT DIFFERENCE
RSD	- RELATIVE STANDARD DEVIATION
TOX	- TOTAL ORGANIC HALOGENS
ppb	- PARTS PER BILLION
ppt	- PARTS PER TRILLION
AA	- ATOMIC ABSORPTION
GC	- GAS CHROMATOGRAPH
GC/MS	- GAS CHROMATOGRAPH/MASS SPECTROMETER
CLP	- CONTRACT LABORATORY PROGRAM

*What samples &
do these
procedures
apply to?*

**PROCEDURES FOR ORGANOCHLORINE PESTICIDES
AND PCBs IN ENVIRONMENTAL MATRICES
REVISED AUGUST 1986**

1.0 INTRODUCTION

1.1 The following procedures are for organochlorine pesticides and PCBs in environmental matrices. The procedures are applicable to the pesticides and PCBs listed in Table 1. The procedures are gas chromatographic (GC) methods written for use at the laboratory bench level. As such, a space is provided on the right hand side for notes and comments.

*I thought
ETC was doing
2nd 11-1000
using CLP method.*

2.0 METHODOLOGY

2.1 The procedures are adopted from methods developed by EPA and State organizations. The principal source of reference is the EPA Contract Laboratory Protocol (CLP) which has also been adopted by NYS DEC for its Superfund programs.

2.2 It is not the intent of this document to rewrite the procedures developed by EPA with the same degree of detail. Instead, our purpose is to adopt the EPA procedures to our operation. As such, it is important that the analyst reads and becomes familiar with the EPA procedures as well as this document. The referenced procedures are copied and attached for your review.

*Will note in
method copies
these methods
ad.*

2.3 Other referenced materials include the EPA Method 608 which is designed for industrial and municipal discharges. Also, a copy of the "Guidelines on Analytical Methodology for Pesticide Residue Monitoring" is attached for your review. This document provides a broader perspective of pesticide analysis.

2.4 Incorporated into this document by reference is the safety section of The 16th Edition of Standard Methods, Section 108. This is mandatory reading in the laboratory.

3.0 NOTES ON THE PROCEDURES

3.1 All glassware must be specially cleaned for trace organics work. The washing procedure is outlined in detail in Appendix 1.

4.0 EXTRACTION PROCEDURE FOR SOLID MATRICES

4.1 Thoroughly homogenize the sample by mixing with a stainless steel spatula. In some cases, it may be necessary to transfer the sample to a blender or ball mill to ensure complete homogenization.

4.2 Weigh a 30 gram portion into a tared pint extraction jar and add 60 grams of anhydrous sodium sulfate. Mix thoroughly with the spatula used to originally transfer the sample. The sample should have a sandy texture at this point. Immediately add 100ml of 1:1 methylene chloride/acetone to the sample.

4.3 At this point, add the appropriate surrogate. For low level determinations add 100ul of the 20ppm dibutyl chlorendate stock prepared in methanol (2ug). For high level determinations, add 100ul of 300ppm DBC stock (30ug). Surrogates are added to blanks, spikes and samples.

4.4 Place the Teflon-lined cap on the extraction jar and shake vigorously. Place extraction jar in auto-shaker and shake for thirty minutes. Allow the solid matrix to settle to the bottom, then decant the solvent extract into a second collection jar. You may prefer to transfer the extract using a disposable 25ml pipet. Repeat the extraction two more times with two additional 100ml portions of 1:1 methylene chloride and acetone. If a clear solvent layer is not achieved for each extraction, the entire extraction jar may be centrifuged between each extraction.

4.5 For low level analysis, pour the solvent extract from the collection jar through a funnel packed with sodium sulfate into a Kuderna-Danish (K-D) concentrator. Add 50ml of hexane to the collection jar and also pass it through the sodium sulfate into the K-D flask. Add 2 or 3 boiling chips, insert a 3-ball Snyder column, prewetted with hexane, and concentrate the extract to ± 5 ml on a steam bath. Proper evaporation is achieved when the balls in the Snyder column actively chatter, but do not flood with solvent. Remove the 3-ball Snyder column and add an additional 50ml of hexane and concentrate to ± 2 ml.

4.6 Disconnect the 10ml ampule from the K-D flask rinsing with small portions of hexane. Bring the final volume to 10ml with hexane. Transfer 1ml of extract to an auto-injection vial with $\pm 1g$ of activated copper metal. Transfer the remaining 9ml to a Teflon screw cap vial for storage.

4.7 For high level analysis, measure the extract volume in the collection jar, then transfer a 10ml portion to a 10ml ampule. Concentrate the extract to $\pm 0.5ml$ on the nitrogen blowdown apparatus. Adjust final volume to 5ml with hexane. Transfer 1ml of the extract to an auto-inject vial with $\pm 1g$ of activated copper metal.

4.8 During the course of the sample extraction, add a quality control blank, matrix spike (MS) and matrix spike duplicate (MSD) to the batch or to every 20 samples. A blank is the glassware, reagents and surrogate (everything but the sample) and it is designed to monitor contamination from reagents or from the analysts' technique. To prepare a matrix spike and a matrix spike duplicate, select a sample randomly and weigh out 2 additional 30g portions into 2 extraction jars. At the point where surrogates are added spike the MS and MSD as follows:

<u>Low Level Analyses</u>		
Lindane	2ppm	
Heptachlor	"	
Aldrin	"	400ul
Dieldrin	5ppm	
Endrin	"	
4,4-DDT	"	

<u>High Level Analyses</u>		
PCB (any Aroclor)		300ug

4.9 Often soil matrices require some kind of cleanup before GC analysis. Four options are available: macro-florisil cleanup, micro-florisil cleanup, alumina column cleanup and acid wash.

4.10 The detection limits for the high level and low level analyses are presented in the attached report.



Pesticide/PCB Priority Pollutants

CLIENT DETECTION LIMITS

JOB NO. _____

DESCRIPTION _____

SAMPLE NO.	DATE COLLECTED			DATE REC'D.	DATE ANALYZED		
	Water	Soil(L)	Soil(H)		Water	Soil(L)	Soil(H)
α -BHC	0.05	8.0	100.	4,4'-DDT	0.10	16.0	200.
γ -BHC				Endosulfan Sulfate	0.10	16.0	200.
β -BHC				Endrin Aldehyde			
Heptachlor				Methoxychlor	0.5	80.0	1000.
δ -BHC				Endrin Ketone	0.1	16.0	200.
Aldrin				Chlordane	0.5	80.0	1000.
Heptachlor Epoxide				Toxaphene	1.0	160.0	2000.
Endosulfan I				PCB-1221	0.5	80.0	1000.
4,4'-DDE	0.10	16.0	200.	PCB-1232			
Dieldrin				PCB-1016/1242			
Endrin				PCB-1248			
4,4'-DDD				PCB-1254	1.0	160.0	2000.
Endosulfan II				PCB-1260	1.0	160.0	2000.

Methodology: Federal Register—40 CFR, Part 136, October 26, 1984

Comments:

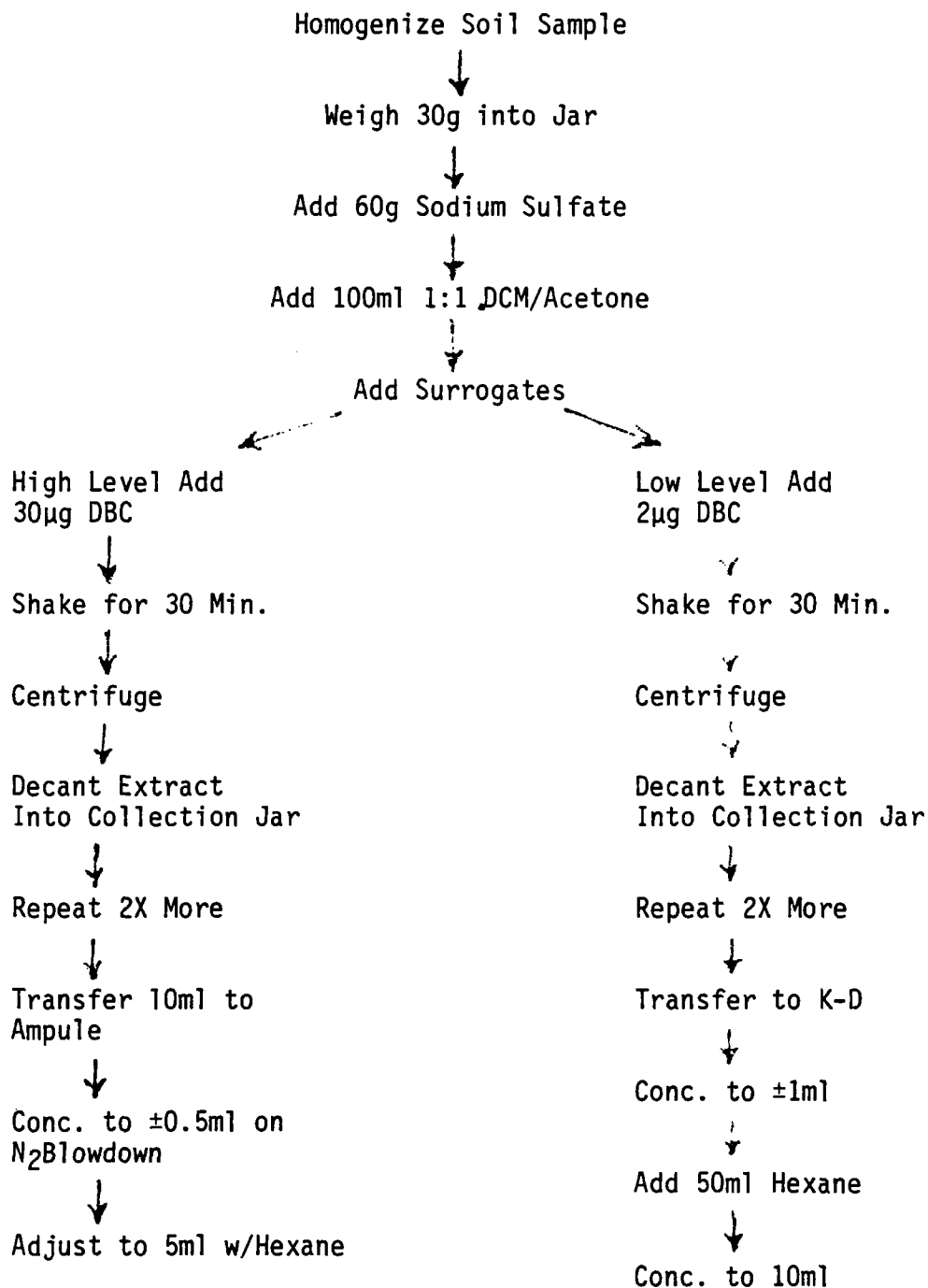
UNITS OF QUANTITATIONWater = $\mu\text{g/l}$ Soil = $\mu\text{g/kg}$ wet weight

Authorized: _____

Date: _____

PESTICIDE + PCBs
EXTRACTION PROCEDURE
FOR SOLID MATRICES

August 1986



5.0 EXTRACTION PROCEDURE FOR WATER SAMPLES

5.1 Mark the meniscus on the side of the sample bottle for later determination of sample volume. Determine pH of sample and adjust to a range of 5-9 with 1:1 sulfuric acid solution or in sodium hydroxide. Pour entire contents of sample bottle into a 2 liter separatory funnel.

5.2 Add 1ml of 1ppm DBC surrogate solution to the sample.

5.3 To every batch of samples or for every 20 samples, add a blank, a matrix spike (MS) and a matrix spike duplicate (MSD). The blank is 1000ml of organic-free water and it is treated in the same manner as the samples. The MS and MSD samples are spiked in duplicate. Ideally, a sample is collected in triplicate in the field in 3 separate containers. The first sample is the sample itself. The second and third samples are spiked with 1ml of the following stock solutions in acetone:

Lindane	0.2ppm
Heptachlor	0.2 "
Aldrin	0.2 "
Dieldrin	0.5 "
Endrin	0.5 "
4,4-DDT	0.5 "

5.4 Add 50ml of 15% methylene chloride in hexane to the sample jar, seal and shake. Transfer bottle extract to separatory funnel and extract the sample by shaking vigorously for 2 minutes with periodic venting to release pressure.

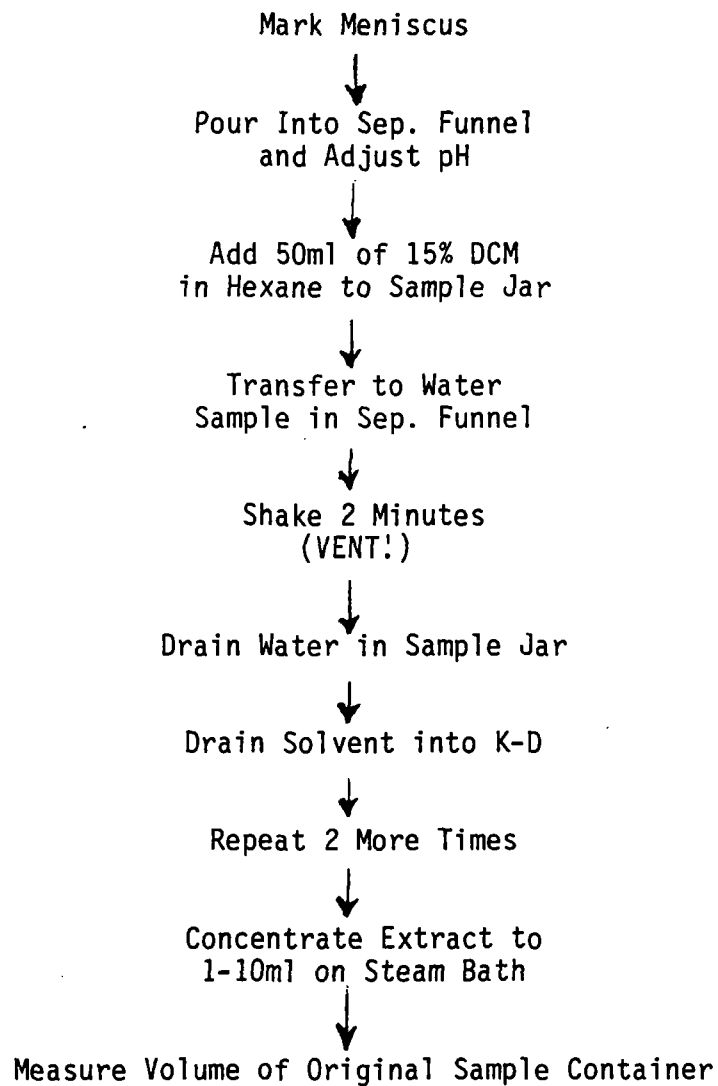
5.5 Drain water sample back into sample jar. Drain the hexane extract through a sodium sulfate funnel into a Kuderna-Danish evaporator. Return water sample back to separatory funnel and repeat extraction 2 more times combining all extracts into the Kuderna-Danish evaporator.

5.6 If emulsion problems occur during extraction, collect all 3 extracts in a 200ml centrifuge bottle without sodium sulfate drying. Centrifuge the contents of the bottle until 2 distinct layers are formed. Transfer the top layer (the hexane extract) through sodium sulfate into the Kuderna-Danish evaporator.

*I thought
ETC were
analyzing for
pesticides.*

PESTICIDES + PCBs
EXTRACTION PROCEDURE
FOR WATER MATRICES

August 1986



**6.0 EXTRACTION PROCEDURE FOR FISH FOR ORGANO-CHLORINE
PESTICIDES + PCBs**

6.1 Depending upon the species of fish or upon the specifications of the program, the fish is either analyzed as a whole, filleted with skin on or skin off. The filleting procedure is as follows:

Clean, scale and eviscerate fish. Take 1" thick slice, one from behind the pectoral fins, one from half way between first slice and the vent, and one from behind vent. Remove bones from each slice before combining.

*no not accepted
The whole fillet
must be processed*

6.2 The fillets or whole fish is chopped into 1" chunks and then frozen. The frozen chunks are ground in a meat grinder and the resulting ground fish is mixed and homogenized, then stored frozen. It is imperative that the filleting tools, grinder and other utensils are thoroughly washed and rinsed with acetone between samples.

6.3 Weigh a 10g portion of the frozen ground fish into a vitris beaker and add 20g of sodium sulfate. Homogenize the mixture using the vitris homogenizer. The resulting mixture should be dry and granular. Quantitatively transfer the homogenized mixture into a glass fritted Soxhlett thimble with a glass wool plug on the top and bottom. Place the thimble in the Soxhlett extractor which contains 200ml of 1:1 acetone and hexane in the receiving flask. Heat and reflux for 8 hours (overnight) and allow to cool to room temperature.

6.4 Rinse the condenser and Soxhlett chamber with hexane into the receiving flask, add a few boiling chips and a 3-ball Snyder column and concentrated extract to approximately 1-2ml on a steam bath. Prewet the 3-ball Snyder column with hexane before refluxing, proper concentration is achieved when the balls in the Snyder column actively chatter, but do not flood with solvent.

6.5 Quantitatively transfer the extract to a 10ml ampule using hexane washes. Adjust the final volume to 5ml. Quantitatively transfer 2.5ml of extract to a tared flask. Strip the solvent and gravimetrically determine lipid content.

6.6 Proceed to Section 7.0 for cleanup prior to GC analysis.

7.0 FLORISIL COLUMN CLEAN-UP (MACRO COLUMN)

7.1 Florisil column chromatography effectively removes interfering organics from the sample extract and roughly separates the pesticides into polar and nonpolar fractions. The pesticide separation profiles achieved by this technique are presented in Figures 2-1 through 2-4. The analyst must demonstrate this same degree of separation for each new batch of florisil used. The procedure for its verification is to run 1ml of a 20ppm mixture of pesticides through a column packed with the new lot of florisil. The eluates are collected in 50ml fractions and directly analyzed on the GC, however, the eluates of 100% methylene chloride must be solvent switched to hexane first.

7.2 To prepare the column, place a small glass wool plug at the base of an 11 X 500mm glass chromatographic column. Dry pack the column with 10g of 60/120 mesh florisil, PR grade, and another inch of anhydrous sodium sulfate. Tap column lightly until evenly packed.

7.3 Pre-elute column and wash with 50ml of hexane. Prior to the exposure of sodium sulfate layer to air, add 1-5ml of the sample extract to the column. Again, just prior to the exposure of the sodium sulfate layer to air, add 100ml of 10% methylene chloride in hexane. Collect eluate, fraction 1, into a 250ml Kuderna-Danish evaporator. Next add 150ml of 100% methylene chloride and collect eluate, fraction 2, into a 250ml Kuderna-Danish evaporator.

7.4 Concentrate both fractions to approximately 2ml in a water bath. Fraction 2 must be solvent switched to hexane by adding 50ml of hexane when the methylene chloride is approximately 2ml, then reconcentrate to desired level.

7.5 Adjust extracts to final volume (usually 1ml) by dilution with hexane or evaporation with a gently stream of purified nitrogen.

7.6 Sulfur interferences usually elute in the first fraction. Add copper metal to extract if sulfur is suspect.

8.0 FLORISIL CHROMATOGRAPHY (MACRO COLUMN)

8.1 Place a glass wool plug in the bottom of a disposable glass Pasteur pipet (1cm O.D. X 5 3/4" long). Add 1.5 grams of florisil and tap gently. Add 0.5 grams of sodium sulfate leaving at least an inch of space in the top of the pipet.

8.2 Pre-elute the column with 10ml of hexane and discard. Just prior to the exposure of the sodium sulfate to air, add 1-2ml of the extract to the column. Again, just prior to the exposure of the sodium sulfate to air, add 10ml of hexane in incremental quantities.

8.3 Concentrate the cleaned extract to 1ml of the nitrogen blowdown apparatus.

8.4 This cleanup procedure effectively separates the nonpolar PCBs from polar organics. However, it also removes the DBC surrogate from the extract.

9.0 ALUMINA COLUMN CLEANUP

9.1 Add 3gm of Activity III neutral alumina to the 10ml chromatographic column (K-420160). Tap to settle the alumina.

9.2 Transfer 1ml of the extract (which has been adjusted to 50:50 acetone and hexane) to the column. Elute the column with 9ml hexane.

9.3 Concentrate to 1ml on the nitrogen blowdown apparatus.

9.4 Add copper metal to the extract if sulfur is suspected.

10.0 SULFURIC ACID CLEANUP (PCB ONLY)

10.1 Transfer 5ml of the extract to a 12ml glass vial with a Teflon liner. The extract must be hexane or iso-octane for the procedure to work.

10.2 Add 5ml of concentrated sulfuric acid to the vial.

10.3 Vortex for 1 minute, then allow the phases to separate.

10.4 Vial 1ml of the organic extract for analysis.

10.5 This procedure will destroy the DBC surrogate if present.

11.0 GAS CHROMATOGRAPHY

11.1 The proper operation of a gas chromatograph requires several years of experience. An analyst becomes proficient by learning from his colleagues, by reading literature and by attending training seminars. Some of the fundamentals of GC analyses are described in the following sections. For the specifics, consult the EPA CLP Protocol.

11.2 Samples processed for pesticides and PCBs are analyzed on a mixed phase polar column. Samples requiring only PCBs are analyzed on a nonpolar column. The instrument conditions are as follows:

Column: 1.5% SP2250 + 1.95% SP2401 on 100/120 Supelcoport packed in a 6ft. X 4mm ID glass column
Oven Temperature: 160°C to 200°C at 20° per minute, 1 minute initial hold

Column: 3% OV-1 on 80/100 Supelcoport packed in a 6ft. X 2mm ID glass column
Oven Temperature: 160°C to 200°C at 10° per minute, 1 minute initial hold

11.3 The presence of a pesticide or PCB in a sample is determined by the retention time of the compound(s) on the GC column compared to the retention time of the standard(s) run under identical conditions. It is, therefore, imperative that the retention times of the standard and samples be reproducible throughout the run period. This is verified in two ways. DBC is added to every sample and to the standards so the retention time of DBC is used as an index. The second method of verification is to run standards in the beginning, in the middle and at the end of the run period.

11.4 If a pesticide is detected in a sample, its presence must be confirmed by analysis on a different column or by GC/MS techniques. In most case, the primary column is the 1.5% SP2250 + 1.95% 2401, a polar column. The confirmation column is the 3% OV-1, a non-polar column. Standards and the sample are analyzed consecutively for confirmation.

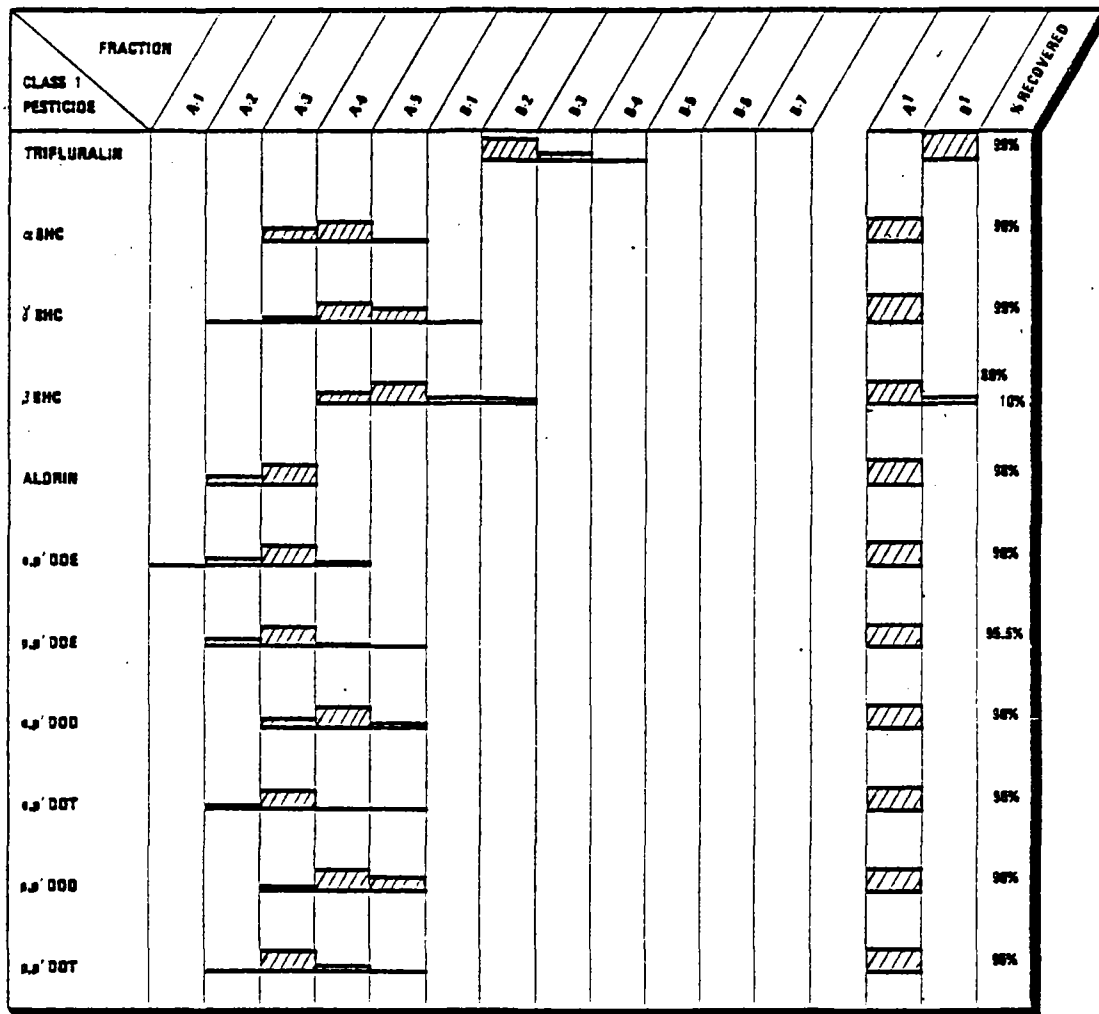


LABORATORY PROCEDURE

11.5 For every batch analysis the linearity of the instrument must be defined by running three standards at three concentration levels. The response factors from these three runs must be within 10% of each other. If a pesticide or PCB is detected in a sample, it must be diluted into the linear range before it is quantitated.

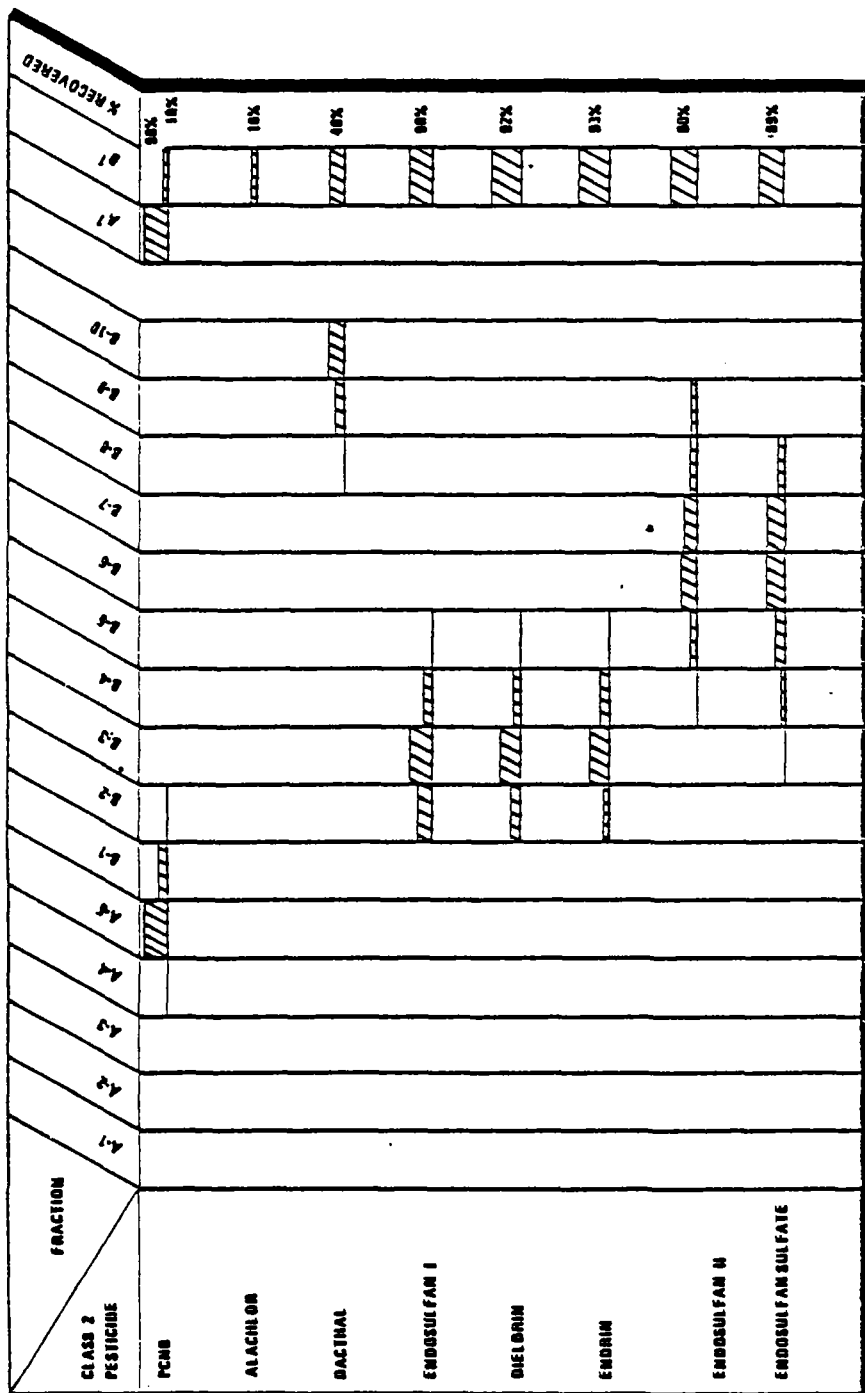
12.0 REFERENCES

- a. USEPA Contract Laboratory Program, July 1985 Revision
- b. EPA Method 608, Federal Register, 40CFR, Part 136, October 26, 1984
- c. Standard Methods for the Examination of Water and Wastewater, 16th Edition, APHA, AWWA, WPCF, 1985
- d. Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue, EPA 600/4-81-055
- e. Food and Drug Administrations Pesticide Analytical Manual, Volume 1, March 1, 1975
- f. Guidelines on Analytical Methodology for Pesticide Residue Monitoring, Federal Working Group on Pest Management, Washington, D.C., June 1975
- g. Organochlorine Pesticides and PCBs in Fish Tissue Samples, Michigan Department of Natural Resources, Received June 28, 1985



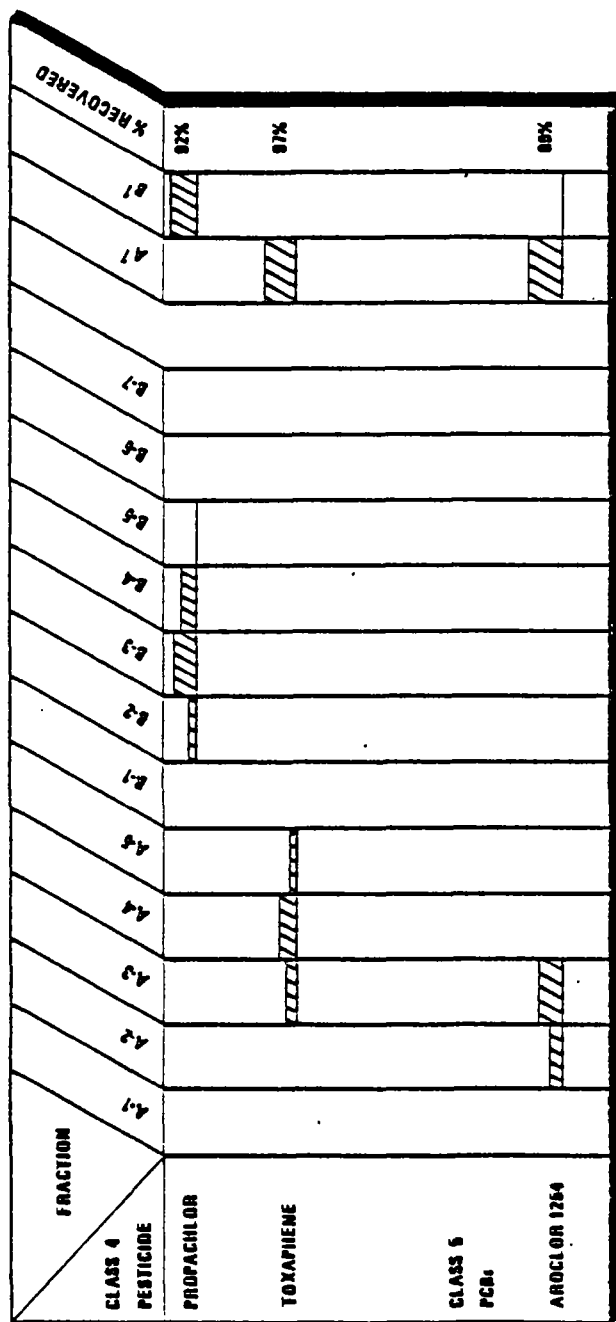
A = 100 ml OF 10% CH_2Cl_2 / 90% HEXANE (20 ml FRACTIONS)
 B = 150 ml OF 100% CH_2Cl_2 (20 ml FRACTIONS)
 A' = 100 ml OF 10% CH_2Cl_2 / 90% HEXANE COLLECTED AS ONE FRACTION
 B' = 150 ml OF 100% CH_2Cl_2 COLLECTED AS ONE FRACTION

FIGURE 2-1
FLORISIL COLUMN PROFILE



A - 100 ml of 10% CH₂Cl₂ / 90% HEXANE (20 ml FRACTIONS)
 B - 200 ml of 10% CH₂Cl₂ / 90% HEXANE (20 ml FRACTIONS)
 A' - 100 ml of 10% CH₂Cl₂ / 90% HEXANE COLLECTED AS ONE FRACTION
 B' - 200 ml of 10% CH₂Cl₂ / 90% HEXANE COLLECTED AS ONE FRACTION

FIGURE 2-2
FLORISIL COLUMN PROFILE



A - 100 ml OF 10% CH₂Cl₂ / 90% HEXANE (20 ml FRACTIONS)
 B - 200 ml OF 100% CH₂Cl₂ (20 ml FRACTIONS)
 A' - 100 ml OF 10% CH₂Cl₂ / 90% HEXANE COLLECTED AS ONE FRACTION
 B' - 200 ml OF 100% CH₂Cl₂ COLLECTED AS ONE FRACTION

FIGURE 2-4
FLORISIL COLUMN PROFILE

CLASS 3 PESTICIDE	FRACTION														X-RECOVERED
	A-1	A-2	A-3	A-4	A-5	B-1	B-2	B-3	B-4	B-5	B-6	B-7	A'	B'	
HCB															82%
HEPTACHLOR															81%
ISODRIN															94%
HEPTACHLOR EPOXIDE															92%
γ CHLORDANE															85%
α CHLORDANE															85%
OVEX															93%
MIREX															82%
METHOXYCHLOR															113%

A = 100 ml OF 10% CH₂Cl₂ / 90% HEXANE (20 ml FRACTIONS)

B = 200 ml OF 100% CH₂Cl₂ (20 ml FRACTIONS)

A' = 100 ml OF 10% CH₂Cl₂ / 90% HEXANE COLLECTED AS ONE FRACTION

B' = 200 ml OF 100% CH₂Cl₂ COLLECTED AS ONE FRACTION

GLASSWARE WASHING PROCEDURE FOR TRACE ORGANICS GLASSWARE

The cleaning procedure for general glassware is as follows:

- Start with a hot soap and water wash contacting all glassware surfaces with a brush..
- Thoroughly rinse with hot tap water. Do not allow glassware to dry with soap residue.
- Soak glassware in hot RBS-35 surfactant solution for 30 minutes.
- Thoroughly rinse with hot tap water. Do not allow glassware to dry with surfactant still on it.
- Rinse interior of each piece of glassware with two portions of acetone (10-50 ml).
- Air dry and wrap openings with aluminum foil for storage.

The cleaning procedure for pipets is as follows:

- Thoroughly rinse pipet with appropriate solvent immediately after use.
- Place on RBS surfactant solution for soaking.
- Rinse with tap water via the automatic syphoning unit.
- Soak in hot RBS surfactant solution for 30 minutes.
- Rinse with tap water via the automatic syphoning unit.
- Rinse with acetone and air dry.

The cleaning procedure for miscellaneous pieces, i.e. teflon stockcocks, is as follows:

- Soak in RBS solution during the period of time between use and washing.
- Start with hot soap and water wash contacting all surfaces with a brush.
- Place on the dip rack of siphoning unit and rinse thoroughly with tap water.
- Soak in hot RBS solution for 30 minutes.
- Rinse again with tap water.
- Transfer pieces to large clean beaker and rinse 3 times with acetone and air dry.
- Rubber O-rings should not be acetone rinsed.

TABLE 1
CRAB ORCHARD REFUGE
SAMPLING SITES

<u>Site #</u>	<u>Type</u>	<u>Name</u>
<u>Group 1</u>		
3	Landfill	Area 11 South Landfill
4	Landfill*	Area 11 North Landfill
5	Pond	Area 11 Acid Pond
<u>Group 2</u>		
7	Surface Water	D Area SE Drainage
7A	Surface Soil	D Area North Lawn
8	Surface Water	D Area SW Drainage
9	Surface Water	P Area NW Drainage
10	Surface Water	Waterworks North Drainage
11	Surface Water	P Area SE Drainage
11A	Surface Soil	P Area North
20	Surface Water	D Area South
<u>Group 3</u>		
12	Landfill*	Area 14 Landfill
13	Surface Soil	Area 14 Change House Site
14	Surface Water	Area 14 Solvent Storage
<u>Group 4</u>		
15	Pond	Area 7 Plating Pond
16	Surface Soil	Area 7 Industrial Site
<u>Group 5</u>		
17	Landfill	Job Corps Landfill
<u>Group 6</u>		
18	Surface Soil	Area 13 Loading Platform
19	Surface Soil	Area 13 Bunker 1-3
30	Control*	Munition Control Site
<u>Group 7</u>		
21	Landfill	Southeast Corner Field
<u>Group 8</u>		
22	Surface Water	Old Refuge Shop
24	Surface Water	Pepsi-West
25	Surface Water	COC at Marion Landfill
26	Surface Water	COC below Marion STP
27	Surface Water	COC below 157 Dredge Area

Attachments



O'BRIEN & GERE

ATTACHMENT 1

ANALYTICAL PROTOCOLS FOR EXPLOSIVES IN SOIL

METHOD NO.: 8H

DATE: 4-21-83

EXPLOSIVES IN SOIL BY HPLC

APPLICATION: Determination of the following nitro-compounds in soil.

HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
RDX	Hexahydro-1,3,5-trinitro-s-triazine
NB	Nitrobenzene
1,3-DNB	1,3-Dinitrobenzene
1,3,5-TNB	1,3,5-Trinitrobenzene
2,4-DNT	2,4-Dinitrotoluene
2,6-DNT	2,6-Dinitrotoluene
2,4,6-TNT	2,4,6-Trinitrotoluene
Tetryl	2,4,6-Trinitrophenylmethylnitramine

A. Tested Concentration Range:

HMX	0.376-188	ug/g
RDX	0.253-127	ug/g
NB	0.197-98.4	ug/g
1,3-DNB	0.242-121	ug/g
1,3,5-TNB	0.215-107	ug/g
2,4-DNT	0.240-120	ug/g
2,6-DNT	0.217-109	ug/g
2,4,6-TNT	0.301-151	ug/g
Tetryl	0.265-133	ug/g

B. Sensitivity: Peak height near the detection limit. (1 mm = 28 arbitrary units on the integrator readout.) Representative chromatogram near the detection limit can be found in Appendix I.

Peak Height in mm at an Attenuation of 2-2

HMX	12 mm for 0.754 ug/g
RDX	18 mm for 0.506 ug/g
NB	11 mm for 0.394 ug/g
1,3-DNB	23 mm for 0.485 ug/g
1,3,5-TNB	20 mm for 0.430 ug/g
2,4-DNT	16 mm for 0.480 ug/g
2,6-DNT	9 mm for 0.434 ug/g
2,4,6-TNT	19 mm for 0.602 ug/g
Tetryl	10 mm for 0.530 ug/g

C. Detection Limits:

HMX	0.376 ug/g
RDX	0.474 ug/g
NB	0.197 ug/g
1,3-DNB	0.242 ug/g
1,3,5-TNB	0.231 ug/g
2,4-DNT	0.240 ug/g
2,6-DNT	0.217 ug/g
2,4,6-TNT	0.301 ug/g
Tetryl	0.265 ug/g

D. Interferences:

1. Any compound that is extracted from soil that gives a retention time similar to the nitro-compounds and absorbs U.V. at 250 nm.
2. Millipore GFWP-01300 filter type GS pore size 0.22 micrometers dissolve in the solvent used.
3. Tetryl and 2-amino-4,6-dinitrotoluene coelute. If a tetryl peak is found in samples, pH adjustment is necessary to separate the peaks to determine which compound is present.
4. 2,4,6-Trinitrobenzaldehyde decomposes rapidly in water solution. Once the acetonitrile standard is made into mobile phase this becomes a problem.

E. Analysis Rate:

After instrument calibration, one analyst can analyze two samples in one hour. One analyst can conduct sample preparation at a rate of three samples per hour. One analyst doing both sample preparation and the HPLC analysis can run 16 samples in an 8-hour day.

II. CHEMISTRY:

A. Chemical Abstracts Service Registry Number:

HMX	2691-41-0
RDX	121-82-4
NB	98-95-3
1,3-DNB	99-65-01
1,3,5-TNB	99-35-4
2,4-DNT	121-14-2
2,6-DNT	606-20-2
2,4,6-TNT	118-96-7
Tetryl	479-45-8

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I. Chemical Reactions:

1. RDX and HMX can undergo alkaline hydrolysis.
2. RDX and HMX degrade at temperatures greater than 80°C in an organic solvent.

II. Physical Properties:

	Formula	Mol. Wt.	M.P.(°C)	B.P.(°C)
HMX	$C_4H_8N_8O_8$	296.16	276	-
RDX	$C_3H_6N_6O_6$	222.12	205	-
NB	$C_6H_5NO_2$	123.11	6	211
1,3-DNB	$C_6H_4N_2O_4$	168.11	90	302
1,3,5-TNB	$C_6H_3N_3O_6$	213.11	122	315
2,4-DNT	$C_7H_6N_2O_4$	182.14	71	300 (decomposes)
2,6-DNT	$C_7H_6N_2O_4$	182.14	66	-
2,4,6-TNT	$C_7H_5N_3O_6$	227.13	82	240 (decomposes)
Tetryl	$C_7H_5N_5O_8$	287.15	131	187

III. APPARATUS:

- A. Instrumentation: Perkin Elmer series 4 High Performance Liquid Chromatograph (HPLC) equipped with a Perkin Elmer ISS-100 Auto-Injector and Perkin Elmer variable wavelength detector LC-75. Hewlett Packard 3390 recording integrator in peak height mode was used to record the data output.

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3. Parameters:

1. Column: Two columns are used in series, in the order listed.

- a. DuPont Permaphase^R ODS guard column.
- b. DuPont Zorbax^R ODS 4.6 mm i.d. x 25 cm HPLC column with a particle size of 5-6 microns.

2. Mobile Phase: The water/methanol ratio must be adjusted as described in the calibration Section V C to obtain optimum peak separation.

44-50% water
28-34% methanol
22% acetonitrile

3. Flow: 1.6 mL/min with a pressure of approximately 2860 psig.

4. Detector: 250 nm

5. Injection Volume: 50 uL.

6. Retention Times: Minutes

HMX	3.38
RDX	4.21
NB	7.33
1,3 DNB	6.63
1,3,5-TNB	5.74
2,4-DNT	9.89
2,6-DNT	9.50
2,4,6-TNT	8.93
Tetryl	7.98

C. Hardware/Glassware:

1. Syringes: 25 uL, 50 uL, 100 uL, 250 uL,
5 mL gas tight syringe (Hamilton 1005 TEFL)
2. Serum vials with crimp caps and Teflon-lined septa
Nominal volume of 0.25 mL, 1 mL, 5 mL.
3. Pasteur pipettes and disposable micropipettes.
4. 13 mm stainless steel syringe filter holder
(Rainin Instrument Co., Inc. #38-101)

C. Hardware/Glassware: (continued)

5. 13 mm x 0.5 micron fluorocarbon filter
(Rainin Instrument Co., Inc. #38-103 Zefluor disc)
6. Whatman 10 mm glass microfiber prefilter
7. U.S. Sieve series 600 (30 mesh)
8. Aluminum foil pans
9. Liquid chromatograph column 1" o.d. x 12"
10. 2 mL, 3 mL, and 5 mL pipettes

D. Chemicals:

1. Acetonitrile, distilled in glass for HPLC use
2. Methanol, distilled in glass for HPLC use
3. Ethyl Ether, distilled in glass for HPLC use
4. Hexane, distilled in glass for HPLC use
5. ASTM Type II Water
6. SARMS for the nitro-compounds

3. STANDARDS: All concentrations are based on a stock solution concentration of 2000 mg/L. Appropriate adjustments should be made if actual concentration varies from this figure.

A. Calibration Standards:

1. Stock Calibration Standards: Stock solutions containing approximately 2000 mg/L of a nitro-compound are prepared by accurately weighing 10 mg of a SARM into a 5 mL serum bottle and dissolving the nitro-compound in 5 mL of acetonitrile pipetted into the bottle. All compounds appear to be stable for 3 months.
2. Intermediate Calibration Standards: All compounds appear to be stable for 3 months.
 1. Intermediate Calibration Standard A (high level): Add the following volumes of stock calibration standard and seal with a Teflon-lined septum cap. Store in the dark @ 0°-4°C. The resulting solution (5.8 mL) will have the concentrations indicated in the following table.

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EXPLOSIVES IN SOIL BY HPLC

A. Calibration Standards: (continued)

Intermediate Calibration Standard A

Nitro-compound	Amt. (uL) of Stock Cal. Std. to add	Resulting conc. (ug/mL)
HMX	1000	345
RDX	600	207
NB	400	138
1,3-DNB	500	172
1,3,5-TNB	500	172
2,4-DNT	500	172
2,6-DNT	500	172
2,4,6-TNT	700	241
Tetryl	600	207
TNBA*	500	172

*2,4,6-Trinitrobenzaldehyde was originally included for certification. However, the compound is too unstable in water solutions to obtain reproducible certification data. It was included in this table as it affects the total volume used to calculate concentration of the other nitro-compounds.

b. Intermediate Calibration Standard B (low level):

Pipette 4.5 mL of acetonitrile into a 5-mL serum vial. Add 500 uL of Intermediate Calibration Standard A. Seal with a Teflon-lined septum cap and store in the dark @ 0-4°C. The resulting solution (5.0 mL) will have the concentrations indicated in the table below:

Intermediate Calibration Standard B

Nitro-Compound	Resulting conc. (ug/mL)
HMX	34.5
RDX	20.7
NB	13.8
1,3-DNB	17.2
1,3,5-TNB	17.2
2,4-DNT	17.2
2,6-DNT	17.2
2,4,6-TNT	24.1
Tetryl	20.7

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EXPLOSIVES IN SOILS BY HPLC

A. Calibration Standards: (continued)

3. Working Calibration Standards: To a series of ten 5-mL serum vials, approximately one gram of prepared soil (see section V.B.) is accurately weighed into each vial. Using a syringe, the volumes of intermediate standard solutions indicated in the following table are injected onto soil. The serum vial is covered with a septum and shaken until the soil no longer looks wet (approximately 60 seconds). The septum is removed and the indicated amount (see Table below) of acetonitrile is pipetted onto the soil. The septum is replaced and the cap crimped on the vial. The sealed sample is blended on a vortex mixer for approximately 2-3 minutes. The sample is prepared via the procedure given in this method, to give the target concentrations in the following table.

WORKING CALIBRATION STANDARDS

Vial No.	Amt. (uL)		Amt. (mL) Aceto-Nitrile to Add	Resulting Concentration (ug/g)				NB
	Intermed. Cal. Std. to Add			HMX	2,4,6-TNT	Tetryl	1,3-DNB; 1,3,5-TNB; 2,6-DNT; 2,4-DNT	
	A	B						
1	0	0	2.0	0	0	0	0	0
2	-	12	2.0	0.414	0.289	0.248	0.206	0.166
3	-	24	2.0	0.828	0.578	0.497	0.413	0.331
4	6	-	2.0	2.07	0.145	1.42	1.03	0.828
5	12	-	2.0	4.14	2.89	2.48	2.06	1.66
6	24	-	2.0	8.28	5.78	4.97	4.13	3.31
7	60	-	2.0	20.7	14.5	14.2	10.3	8.28
8	120	-	1.9	41.4	28.9	24.8	20.6	16.6
9	240	-	1.8	82.8	57.8	49.7	41.3	33.1
10	600	-	1.4	207	145	142	103	82.8

- B. Control Spikes: Control spikes are prepared in the same manner as the calibration standards.

C. PROCEDURE:

*NOTE THE FOLLOWING SAFETY PRECAUTIONS:

1. A 5-mL gas tight syringe (Hamilton 1005 TEFL) is used, as the teflon/glass seal is less likely to cause an explosion than glass/glass.

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2. The nitro-compounds are less reactive when wet, so every precaution should be taken to ensure that work areas are kept clean and that solutions are not left unattended and allowed to dry.
3. The filtering apparatus is immersed in a water bath and disassembled under water immediately after use. The danger here is solution getting dried on the threads of the filtering apparatus and detonating.
4. When preparing SARM stock standards from pure compounds which are stored in water, small aliquots are scooped onto a nylon or polyvinylidene chloride filter. The water is vacuum filtered off and an appropriate quantity of the "dried" material is weighed out for stock standard preparation. Any extra compound thus dried is disposed of.
5. Prior to working with explosives, it is advisable to discuss safety/handling/storage requirements with an explosives expert.
- A. Sample Preparation: The soil sample is removed from the sample bottle and spread out in aluminum foil trays. The sample is air dried. The dried soil is screened through a US series 600 sieve (30 mesh). This screened sample is subsampled according to ASTM procedure D346. The moisture content is determined by ASTM Method D2216-71.

B. Extraction:

1. Accurately weigh 1 gram of prepared soil (see section V.A. above) into a 5-mL serum vial, and pipette 2 mL of acetonitrile onto the soil.

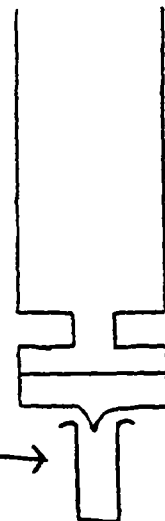
Place a septum and cap on the vial, crimp into place, and shake the vial thoroughly on a vortex mixer for 2-3 minutes.

2. Set up the filtering apparatus, as shown.

5-mL syringe barrel (plunger removed)

5-mL syringe fitted with a Rainin 13 mm stainless steel filter holder with a 10 mm glass microfiber prefilter and a 0.5 micron fluorocarbon filter.

1 mL serum vial to collect filtered sample



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f. PROCEDURE: (continued)

3. Prepare the sample for injection as follows:
 - a. Pour the sample extract into the syringe.
 - b. Place the plunger in the syringe and force at least 500 μ L of the filtrate into a 1-mL serum vial.
 - c. Using a disposable micropipette, accurately measure 200 μ L of filtered extract into a 1-mL serum vial. Accurately measure 600 μ L of a 33% methanol/67% water solution onto the filtered sample. This will produce 800 μ L of extracted sample in mobile phase.
 - d. Place a septum and cap on the vial and crimp into place. Shake the vial well to thoroughly mix. Store in the dark @ 0-4°C until ready to analyze.
4. For samples outside the calibration range, a smaller sample volume is extracted into 5-mL of acetonitrile.
 - a. Accurately weigh 0.2 gram of prepared soil into a 5-mL serum vial, and pipette 5 mL of acetonitrile onto the soil. Place a septum and cap on the vial, crimp into place, and shake the vial thoroughly on a vortex mixer for 2-3 minutes.
 - b. Prepare the sample for injection as follows:
 - 1) Pour the sample extract into the syringe.
 - 2) Place the plunger in the syringe and force at least 3 mL of the filtrate into a 5-mL serum vial.
 - 3) Using a disposable pipette, accurately measure 1 mL of filtered extract into a 5-mL serum vial. Accurately measure 3 mL of a 33% methanol/67% water solution onto the filtered sample. This will produce 4 mL of extracted sample in mobile phase.

Alternately, the sample extract and methanol/water solution may be accurately weighed into a 5-mL serum vial. (1 mL \approx 1 g)

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- 4) Place a septum and cap on the vial and crimp into place. Shake the vial well to thoroughly mix. Store in the dark @ 0-4°C until ready to analyze.
- c. If the solution prepared from the 0.2 g sample is still above the calibration range, make dilutions of the extract obtained in 4b(1) by taking an appropriate aliquot and adding mobile phase (e.g. 100 mg of acetonitrile sample extract in 20 mL mobile phase) to produce a solution within the calibration range of the instrument.

C. Instrument Calibration/Sample Analysis:

1. Using the auto-injector manufacturer's recommended procedure, introduce 50 uL of the 2X working calibration standard into the chromatographic system. Check the chromatogram to ensure separation of the nitrated toluenes and separation of the nitrobenzene and tetryl. If necessary, adjust the water/methanol ratio of the mobile phase until separate peaks are distinguished. As the column ages, less methanol is required. Generally, the column ages rapidly the first 24 hours, after which it is fairly stable.
2. Once good peak separation is obtained, introduce 50 uL of each working calibration standard and sample into the chromatographic system using the auto-injector manufacturer's recommended procedure.

E. CALCULATIONS:

$$A. \text{ Sample Concentration (ug/g)} = \frac{(\text{peak ht.} - K) \times C \times E}{\text{slope} \times A \times B \times D}$$

where:

- K = y-intercept of the calibration curve regression line
- slope = slope of the calibration curve regression line
- A = $\frac{8 \text{ mL mobile phase}}{1 \text{ gram sample}}$ = a constant for this method.

Explanation: the instrument reads the total ug in the 50 uL aliquot of sample injected. This constant enables results to be interpreted as ug/g, as the calibration curve in ug/g is obtained by

$$\frac{2 \text{ mL acetonitrile to extract}}{1 \text{ gram calibration std. sample}} \times \frac{4 \text{ mL mobile phase}}{1 \text{ mL acetonitrile extract}}$$

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7. CALCULATIONS: (continued)

- B = sample weight
C = mL acetonitrile used to extract sample
D = mL acetonitrile extract diluted into mobile phase
E = final volume in mL of mobile phase prepared for injection

NOTE: When samples are prepared the same as the calibration standards (1 gram extracted into 8 mL of mobile phase), the above calculation becomes:

$$\begin{array}{l} \text{Sample} \\ \text{Concentration} \\ \text{(ug/g)} \end{array} = \frac{(\text{Peak height} - K)}{\text{slope}}$$

8. All soils data must be reported on a moisture-free basis. Moisture content is determined by ASTM D2216-71. 100%-% Moisture = % solids.

$$\begin{array}{l} \text{Concentration on a} \\ \text{moisture free basis} \end{array} = \frac{\text{analyte concentration}}{\% \text{ solids}} \times 100$$

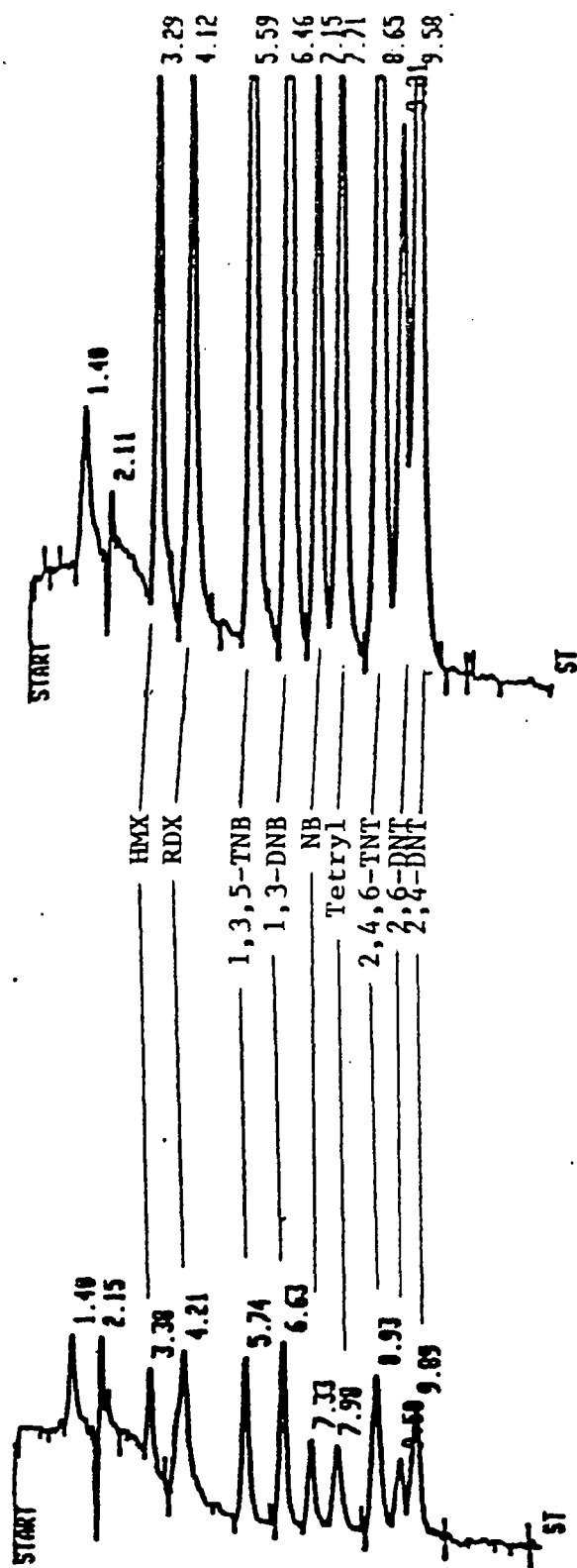
9. REFERENCES:

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EXPLOSIVES IN SOILS BY HPLC

APPENDIX I: CHROMATOGRAMS

EXPLOSIVES IN SOIL - ACETONITRILE EXTRACTION



RUN # 145
ID 1

APR/22/83 12:58:26

HEIGHT	RT
583	1.40
535	2.15
332	3.38
520	4.21
573	5.74
632	6.63
305	7.33
280	7.98
539	8.93
259	9.50
458	9.89

HEIGHT	TYPE	AR/HT
583	VV	0.435
535	PB	0.135
332	VB	0.155
520	BV	0.365
573	PB	0.201
632	BP	0.200
305	PV	0.208
280	VB	0.258
539	BV	0.251
259	VV	0.243
458	VB	0.286

HEIGHT	RT
11.623	1.40
10.666	2.11
6.619	3.29
10.367	4.12
11.423	5.59
12.600	6.46
6.001	7.15
5.582	7.71
10.746	8.65
5.164	9.21
9.131	9.50

HEIGHT	TYPE	AR/HT
596	BV	0.344
444	PV	0.137
2399	PB	0.158
2392	BB	0.207
4384	PB	0.186
4822	PB	0.191
2182	BV	0.193
2206	VB	0.247
3505	BV	0.241
1030	VV	0.227
3441	VB	0.251

RUN # 148
ID 1

APR/22/83 14:04:05

HEIGHT	RT
2.107	1.40
1.570	2.11
8.483	3.29
8.438	4.12
15.582	5.59
17.050	6.46
7.715	7.15
8.003	7.71
12.355	8.65
12.355	9.21
12.355	9.50

ATTACHMENT 2

ANALYTICAL PROTOCOLS FOR DIOXINS AND DIBENZOFURANS

ACKNOWLEDGMENT

Thanks J. C. T. Hollander for helpful discus-

No. H₂SO₄, 7664-93-9.

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Determination of Part-per-Trillion Levels of Polychlorinated Benzofurans and Dioxins in Environmental Samples

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National Fisheries Research Laboratory, U.S. Fish and Wildlife Service, Route 1, Columbia, Missouri 65201

A new analytical method permits determinations of parts-per-trillion levels and lower of tetrachloro through octachloro dibenzo-*p*-dioxins and dibenzofurans in various environmental tissues and sediments. Preliminary tests indicated the method is applicable to determinations of polychlorinated biphenyls. Interferences both from natural and from xenobiotic substances are reduced to extremely low levels. The procedure has an extremely low susceptibility to false-positive determinations which could result from the presence of a wide variety of cocontaminants. This approach to contaminant enrichment has permitted reduction of seven processes into a two-step procedure, substantially reducing time requirements and the number of sample manipulations, and making the procedure amenable to automation. The reliability and accuracy of the procedure is demonstrated by the results of intralaboratory and interlaboratory studies and by successful analyses of over 200 samples of a wide variety of types.

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and ortho-unsubstituted polychlorinated biphenyls (non-ortho PCBs) are three chemically and toxicologically related families of anthropogenic compounds that have in recent years been recognized to have the potential to cause serious environmental pollution (1-6). These substances are trace-level components of byproducts in several large-volume and widely used chemical processes, principally PCBs and chlorinated phenols, and can also be produced during combustion processes (7, 8) and by photolysis (12, 13). In general, PCDDs, PCDFs, and non-ortho PCBs are classified as highly toxic compounds (14), although the toxicities are dramatically de-

pendent on the number and positions of the chlorine substituents (15). About 10 individual members of a total of 216 PCDDs, PCDFs, and non-ortho PCBs are among the most toxic man-made or natural substances to a variety of animal species (1-4). The toxic hazards posed by these chemicals are exacerbated by their propensity to persist in the environment (16-18) and to readily bioaccumulate (19-21), and although the rate of metabolism and elimination is strongly species dependent (20), certain highly toxic isomers have been observed to persist in the human body for more than 10 years (22).

The majority of scientific and governmental concerns for the hazards of these compounds have been directed toward analytical methodologies, toxicology, epidemiology, and determination of the disposition in the environment of the single most toxic isomer, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) (1-6, 8).

More recently, however, investigations into the formation and occurrence of PCDFs suggest that this family of toxic compounds may commonly occur at comparable or greater levels than and could generally pose a greater hazard than PCDDs. PCDFs are often found as cocontaminants in and are readily produced from pyrolysis of PCBs (7, 23-26). Most important, the PCDFs produced from pyrolysis of PCBs are predominantly the most toxic isomers, those having a 2,3,7,8-chlorine substitution pattern (5). A number of recent fires involving electrical transformers and capacitors have demonstrated the potential for formation of hazardous levels of PCDFs from pyrolysis of PCBs (26-28, 30).

In light of these findings and because of the dearth of data pertaining to the occurrence of these compounds in the environment, PCDFs and non-ortho PCBs were included as target compounds in a proposed survey by this laboratory of important U.S. rivers and lakes for PCDDs. The decision to include as many PCDD isomers as possible was based on

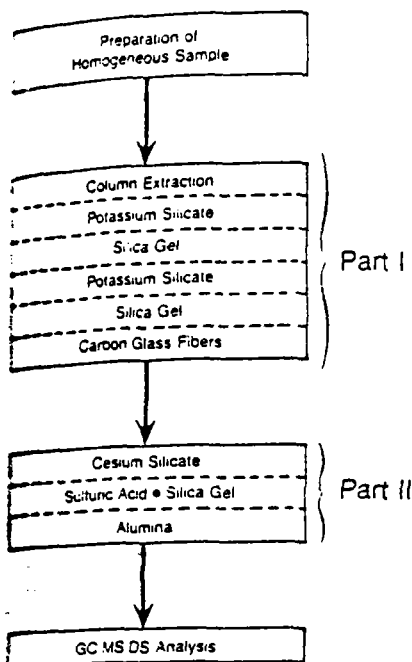


Figure 1. Flow chart of total procedure.

(1) several other PCDD isomers are also ex-
 (15); (2) pentachlorophenol, a large-volume
 and wood preservative, contains relatively high levels
 hepta- and octachlorodibenzodioxins and essentially
 CDDs (7, 8, 29); and (3) incineration of materials con-
 chlorophenols readily produces mixtures of PCDDs,
 TCDD is a minor component. On the other hand,
 toxic 1,2,3,7,8-pentachloro isomer is a major com-
 PCDD incineration products of pentachlorophenol
 Component-specific analyses can be a crucial link to
 source of contamination because different sources of
 and PCDFs usually produce mixtures of distinctly
 relative component abundances (7). On the other
 the preferential accumulation of certain isomers in
 may prevent source identification from analyses of
 equal samples.

critical method developed for this investigation was
 to meet six criteria: (1) permit determinations of
 of these compounds, especially those possessing
 than three chlorine substituents; (2) permit isomer-
 determinations of the most toxic or otherwise im-
 components; (3) provide a lower limit of detection for
 components of between 1 and 5 parts per trillion
 a variety of environmental samples; (4) generate data
 acceptable and adequately defined level of accuracy
 precision; (5) exhibit a very low and well-defined sus-
 to interference and false-positive determinations;
 minimize analyst's time requirements to permit
 of large numbers of samples.

determinations of PCDDs and PCDFs demand an unusu-
 level of analytical assurance, not only because of the
 hazards of these compounds, the intensity of public
 safety concern, and the widespread nature of the
 but also because of the great difficulties in rigorous
 of individual isomers. These difficulties are not
 related to the problems of distinguishing between
 this problem is essentially solved (31-34)—but are
 to the possibility of specific and nonspecific inter-
 from natural and especially xenobiotic substances

herein are the description of an analytical method
 of validation and applications studies which
 the accuracy and reliability and demonstrate the utility

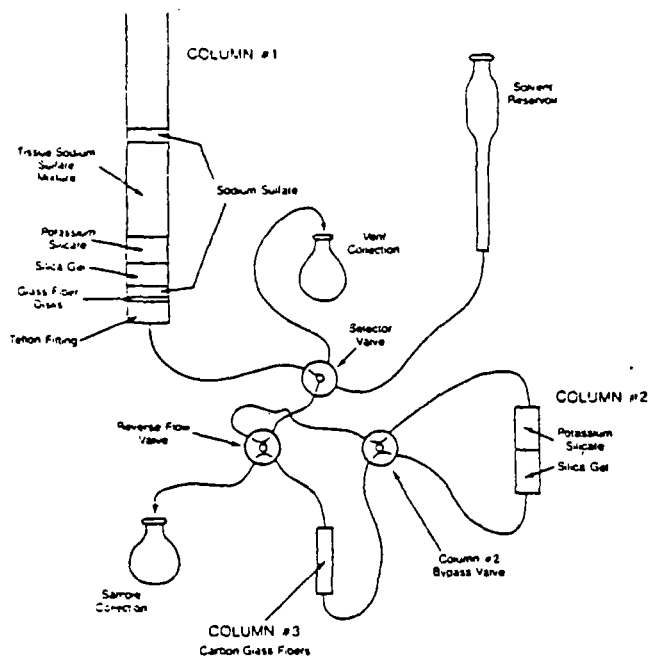


Figure 2. Schematic of part I enrichment apparatus.

of the method developed for the determination of PCDDs,
 PCDFs, and non-ortho PCBs in a variety of environmental
 matrices.

EXPERIMENTAL SECTION

Enrichment Procedure. Tissue and sediment or soil samples (spiked with isotopic marker compounds) are processed in a two-part enrichment procedure (Figure 1). In part I, a mixture of the sample and sodium sulfate is subjected to solvent extraction, and the extract is, in the same process, passed through a series of silica-based adsorbents and then through the carbon/glass fiber adsorbent. The extract passes through the adsorbents in the following order: potassium silicate, silica gel, cesium or potassium silicate, silica gel, and finally an activated-carbon adsorbent. The residues of interest [PCDDs, PCDFs, and non-ortho PCBs, as well as other chemical classes such as polychlorinated naphthalenes (PCNs), polychlorinated biphenylenes, and certain polynuclear aromatic hydrocarbons] are retained on the carbon adsorbent and subsequently recovered by reverse elution with toluene.

In part II of the procedure, following a change of solvent to hexane, the sample is applied to a second series of adsorbents contained in two tandem columns. The first column contains small amounts of cesium or potassium silicate and sulfuric acid impregnated silica gel. The effluent from this column flows directly onto the second column containing activated alumina on which the final fractionation of several classes of residues is accomplished. Following reduction of sample volume, analyses are carried out by high-resolution gas chromatography/low-resolution mass spectrometry/computer data system analysis (HRGC/LRMS/DS) and under some circumstances by gas chromatography/electron capture detector analysis (GC/EC).

Part I. The components of the apparatus used in part I of the enrichment procedure are depicted in Figure 2. Column 1 (about 4.5 cm i.d. and about 1 m long) is connected to column 2 (22 mm i.d. × 100 mm, Michel-Miller precolumn 5769-34, Ace Glass, Vineland, NJ) and to column 3 (1.0 cm i.d. × 6 cm thick-walled, precision-bore glass tubing, Kontes, Vineland, NJ) by means of standard 1/16 or 1/8 in. o.d. Teflon tubing and tube end fittings. Column 3 is equipped with in-house fabricated Teflon fittings. The solvent flow switching valves are Hamilton miniature inert valves (Hamilton Co., Reno, NV): selector valve (no. 86781), on-off valve (no. 86775), and bypass and reverse-flow valves (no. 86781). The washing solvent reservoir is constructed of a 20-cm length of 12 mm o.d. glass tubing and a 200-mL reservoir fitted with a 24/40 female ground glass joint. The valving arrangement (Figure 2) is designed to enable the analyst to perform the following operations: venting of the solvent line from column 1, venting of the solvent reservoir, bypass of column 2, delivery of

from column 1 to columns 2 and 3 sequentially, solvent from the reservoir sequentially to columns 2 and 3 only, reversal of solvent flow in columns 2 and 3, and reversal of solvent flow in all lines. The solvent is pressurized with 1–10 psi nitrogen during the process. Column 2 is packed with equal volumes, 15 cm each, of potassium silicate and silica gel (EM-60, Whatman Inc.) bracketed by plugs of glass wool or preferably fiber filters (3- μ m retention GF/D, Whatman Inc.). Column 3 is packed with a mixture of Amoco PX-21 carbon and glass fibers as described previously (36). The column is packed in the following sequence: two disks of glass fiber (GF/D, 4.7-cm diameter, Whatman Inc., Clifton, N.J.), 10 cm depth of anhydrous sodium sulfate, 30 g of silica gel (130 °C activated), 30 g of potassium silicate (130 °C activated), 50 g of a 1:4 (w/w) mixture of the sample and anhydrous sodium sulfate, and lastly a 2-cm depth of anhydrous

sulfate. Figure 2 is usually packed with fresh adsorbents but this column can be used for more than one sample. The amounts of extracted materials, such as lipids, are small. The carbon adsorbent in column 3 is routinely reused between samples (under 3–8 psi of nitrogen) between samples by reversing solvent sequence: 100 mL each in reverse flow of methanol, toluene, and cyclohexane/methylene chloride (1:1 v/v). Column 2 is bypassed during these washings. After the final washing with solvent A, which is directed through column 2 in the reverse direction to remove residual air and contaminants. Care must be taken to avoid passing through column 2. Another 100 mL of solvent A is passed through columns 2 and 3 in the forward direction for solvent washing. Complete displacement of toluene from column 3 is essential. After columns 2 and 3 are properly washed, column 1 is loaded with adsorbents and sample, a 100 μ L of marker compounds is applied to column 1 and washed onto the packings with four or five 20-mL portions of solvent A using a Teflon wash bottle. The selector valve is positioned so that column 1 is connected to the flask and air is allowed to escape. The flow of air from column 1 is monitored as it bubbles through solvent at the vent. After the sample is spiked with marker compounds, solvent A is carefully applied to column 1, and the solvent front is observed. As the solvent front reaches the transfer line (about 1 m in length), air bubbles in the line are removed by stopping the flow and tapping the line. When the solvent front reaches the selector valve, the valve is repositioned to direct the extract through columns 2 and 3, and the enrichment procedure is under way. The effluent is collected in a flask positioned above columns 2 and 3 to maintain a positive pressure on these columns. The height of column 1 above the flask is adjusted to produce a solvent flow of not less than 1 mL/min but sufficient to complete the process. Occasionally the solvent flow will slow or stop during the process and will require the application of 1 or 2 psi of nitrogen to the system at column 1. Rarely, the glass fiber at the inlet end of column 3 become clogged during the process of decomposition or very oily (especially lake trout). To reduce these complications, a removable column (1.0 x 3 cm) containing 4 or 5 disks of glass microfibers is placed in line at the exit end of column 2. If this filter becomes clogged, it can be replaced during the process. After completion of the initial extraction/adsorption operation, column 3 (bypassing column 2) is washed in the forward direction with 75 mL of solvent A and then 50 mL of methylene chloride/benzene (75/20/5) at a flow of approximately 1 mL/min. These washings are collected in the flask with the sample. The reservoir is then charged with 40 mL of toluene and passed through the carbon (column 3) in the reverse-flow direction at approximately 2 mL/min and collected in a 100-mL flask (24/40) flask. At this point, part I of the procedure

sample in toluene is subjected to rotary evaporation at a vacuum of about 0.1–0.2 atm. The rotary evaporation must be maintained in an uncontaminated condition. Washings with organic solvents. No lubricating greases. The integrity of the sample is protected during rotary

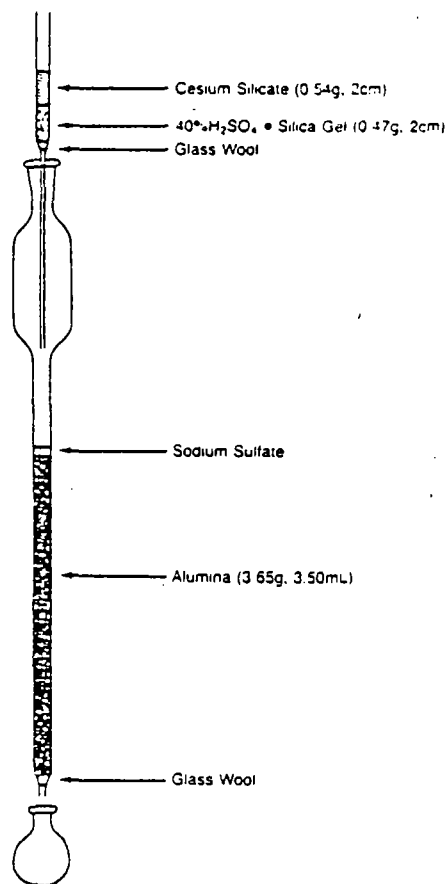


Figure 3. Schematic of part II enrichment procedure.

evaporation by the use of a vapor trap situated between the sample flask and the evaporation apparatus; the vapor trap is thoroughly washed with toluene between samples. The toluene solution (sample) is carefully reduced to less than 1 mL or just to dryness and removed immediately. The solution or dry sample can be stored in a freezer. At this point, the sample is ready for part II of the procedure (after removal of all toluene).

Part II. The apparatus for part II of the enrichment procedure consists of two columns arranged in tandem (Figure 3). Column 4 is prepared from a disposable Pasteur pipet and is packed first with a plug of glass wool, then with 3 cm (0.50 g) of sulfuric acid impregnated silica gel, then with 3 cm (0.54 g) of cesium potassium silicate (not heat activated), and finally with 0.5 cm of anhydrous sodium sulfate. Column 5 is constructed from a 5-mL graduated pipet fitted with a 20-mL reservoir and a ground-glass joint. Column 5 is packed with a plug of glass wool followed by 3.50 mL (3.65 g) activated (190 °C) alumina and then 0.5 cm of anhydrous sodium sulfate. The alumina is packed firmly by sharply tapping the supporting clamp.

Columns 4 and 5 (Figure 3) are thoroughly washed before use, column 4 with 10 mL of hexane and column 5 under approximately 5 psi of nitrogen pressure, with 30–50 mL of hexane to remove entrapped air. Following the washings, column 4 is partly inserted into column 5 so that the effluent from column 4 flows directly onto the adsorbent bed of column 5. A 50-mL collection vessel is placed at the exit end of column 5. Pasteur pipets previously heated for several hours at 500 °C are used for liquid transfers. The sample is applied to column 4 by using four to six separate 1-mL washings (approximate volumes) of hexane totaling 5.0 mL. Each washing is allowed to pass through column 4 and completely onto the alumina of column 5 before the next washing is applied. After 5.0 mL of hexane has passed through column 4, this column is discarded, and a second 5.0-mL volume of hexane is then applied to column 5. The following sequence of eluting solvents is then applied to column 5: 15 mL of 2%, then 15 mL of 5%, and finally 20 mL of 8% methylene chloride in hexane. A total of 60 mL of effluent is thus collected in two fractions, the first measuring 23 mL and the second 37 mL. Due to variations in the activities of different lots of alumina, the

...volumes must be carefully determined for each ... fraction, containing the residues of interest, is ... a volume to about 0.5 mL under a stream of nitrogen ... water bath. The sample is transferred to a conical ... 0.5-mL washings with methylene chloride, each ... reduced to a smaller volume under a stream of ... before the next is added. Following the last transfer, ... is completely evaporated and the appropriate volume ... solvent (usually 10 μ L of toluene or o-xylene) is added ... analysis. If the analysis is to be performed later, the ... be kept in the dry state and stored in a freezer. Before ... is injected, the solution is drawn up into the microliter ... and applied repeatedly to the wall of conical portion of ... being the entire sample into solution. Gas chroma- ... mass spectrometric analyses are carried out by the ... technique (no splitting of the sample) with 2-4 μ L ... volumes or by the on-column technique in which 1-2 μ L ... are injected.

Sample Preparation. Tissue and sediment samples are ... with at least 4 times their weight of anhydrous sulfate. ... samples are first cut into small pieces, ground in a meat ... (if necessary), and mixed thoroughly with anhydrous ... sulfate with a spoon in a glass or polyethylene dish. The ... is then spread out to a depth of less than 3 cm so that ... which solidifies after 3-6 h, can be readily broken up ... overnight. The mixture is then dry-blended (any ... model blender) in a glass jar to yield a fine powder. ... of low water content did not require overnight equilib- ... with sodium sulfate before blending. A second blending ... 4-6 h after the first is often required to produce ... homogeneous and finely divided sample.

Instrumental Conditions and Conditions. Determinations ... and PCDDs were carried out with a Finnigan 4023 ... system equipped with an INCOS data system and with ... and positive chemical ionization options. Methane was ... reagent gas for the negative ion chemical ionization ... The gas chromatograph was usually fitted with either ... 0.25 mm DB-5 fused-silica capillary column (J&W ... Rancho Cordova, CA) or a 55 m \times 0.27 mm Silar ... prepared by H. R. Buser, Swiss Federal Research ... Lucerne, Switzerland. The carrier gas was helium and ... temperature program was routinely used with o- ... 150-255 $^{\circ}$ C at 3 $^{\circ}$ C/min and then 12 $^{\circ}$ C/min to ... and hold for 10 min. The electron impact mode (EI) and ... detection (MID) were routinely used for GC/MS ... and quantitation of PCDFs and PCDDs including ... marker compounds (13 C-TCDD, 37 Cl-TCDF, and ... PCDD). By use of DB-5 column, a series of either 8 or 12 ... ratio (m/z) values were monitored within each ... chromatographic windows, each window being defined ... lower and upper elution limits of a particular group of ... and PCDD congeners. The MID analysis usually involved ... of four or five members of a molecular ion cluster ... of the fragment ion cluster resulting from the ... m/z 63.

... chromatographic analyses employing a packed column [2 ... 3% OV-17 on 100/120 Supelcoport (Supelco, Inc., ... PA)] were carried out on a Varian 3700 gas chroma- ... equipped with an electron capture detector. Nitrogen ... the carrier gas with the following temperature pro- ... 150-270 $^{\circ}$ C at 8 $^{\circ}$ C/min and hold for 15 min.

Materials. All solvents were glass distilled grades (MC/B, ... OH, or Burdick and Jackson, Muskegon, MI). Silica ... 70-230 mesh (EM Reagent, MC/B, Cincinnati, OH) and ... (AG4, Bio Rad Labs, Richmond, CA) were used. ... was washed with methanol and then methylene chloride ... activated at 190 $^{\circ}$ C for at least 2 days. Silica gel was ... in the same manner and activated at 130 $^{\circ}$ C. The silica ... in the 130 $^{\circ}$ C oven and removed just prior to use. ... (MC/B, no. SX760) is heated at 500 $^{\circ}$ C overnight ... in screw capped bottles.

PX-21 activated carbon was obtained from the Amoco ... Center, Naperville, IL 60566, and lot numbers 75-8, ... and 78-10 were successfully used in this laboratory. ... is now commercially available from Anderson De-

velopment Co., Adrian, MI 49221, under the name AX-21.

Potassium and cesium silicates were prepared from the reaction of the corresponding alkali metal hydroxides with silica gel in methanol at 55 $^{\circ}$ C for 90 min. The reaction is carried out in a 1- or 2-L round-bottom flask which is rotated and heated with a rotary evaporation apparatus (no vacuum applied). Sixty grams of CsOH (99+%, Aldrich Chemical Co., Milwaukee, WI) is dissolved in 200 mL of methanol and separated from insoluble material by decantation. An additional 200 mL of methanol is added followed by 100 g of silica gel. For potassium silicate, 168 g of KOH (J. T. Baker Chemical Co., Phillipsburg, NJ), 300 g of silica gel (EM60), and approximately 700 mL of methanol are used; decantation is not necessary for KOH. Following the reaction, the mixture is poured into a large glass column containing a plug of glass wool. Special care must be exercised to avoid contact with the extremely caustic solution, especially eye contact. The adsorbent is washed into the column with methanol, and then 200 mL of methanol for every 100 g of silica gel is added to the column. The methanol can be pushed through the column under slight gas pressure, and as the level of the liquid reaches the bed of adsorbent, 200 mL of methylene chloride for every 100 g of silica gel is applied. The liquid is pushed through the column and the silicate partly or completely dried under a slow flow of nitrogen. Cesium silicate is dried completely under a stream of nitrogen and is not heat activated; potassium silicate is activated at 130 $^{\circ}$ C.

Sulfuric acid impregnated silica gel (40% w/w), abbreviated as SA-SG, is prepared by adding 2 parts of concentrated sulfuric acid to 3 parts by weight of 130 $^{\circ}$ C activated silica gel in a screw capped bottle and shaking until the mixture is completely free of lumps, about 15 min. The silica gel is activated at 130 $^{\circ}$ C; unactivated silica gel is unsatisfactory for the preparation of SA-SG. The adsorbent is stored in a screw capped bottle.

Nitrogen gas used for evaporations of solvents is passed through a copper tube (40 mm o.d. \times 60 cm) containing activated carbon (coconut charcoal, Fisher Scientific Co., Pittsburgh, PA) bracketed by glass wool and glass microfiber filters. Following the carbon trap, a microfiber filter (Microfibre filter 9802-AAQ, 505-AAQ, 0.3- μ m retention, Balston Filter Products, Lexington, MA) is inserted in the line in an attempt to prevent movement of carbon particles through the nitrogen line.

RESULTS AND DISCUSSION

Development and Functions of the Components of the Enrichment Procedure. Part I. A primary objective in the initial approach to the development of this method was to make optimum use of the highly selective absorptivity of activated carbons for polychlorinated polycyclic aromatic compounds (37). The carbon adsorbent selected for this procedure was Amoco PX-21 dispersed in glass fibers (CGF) which has been thoroughly evaluated in this laboratory with regard to its selectivity for a wide variety of chemical classes (36, 37). At least four lots of PX-21 carbon have been successfully employed by this and other laboratories (26, 38-46) in analyses of PCDDs and PCDFs.

Application of extracts of whole fish directly to the carbon adsorbent dispersed in glass fibers was found to be generally unacceptable due to the adsorption of biogenic substances causing high back pressures. Pretreatment of the tissue extract with the strongly basic adsorbent potassium silicate (KS) (47, 48) followed by activated silica gel (SG) greatly facilitated the flow of the tissue extract through the carbon adsorbent. Other combinations with alumina and with Florisil or with potassium silicate alone were less effective. The combination of KS, SG, and PX-21 carbon adsorbents achieved a very high degree of enrichment of PCDDs, PCDFs, and non-ortho PCBs. Tissue samples up to 50 g and containing 10-20 g of fat routinely give only submilligram residues in the sample recovered by reverse elution of the carbon with toluene. Integration of these three steps yielded a procedure that permitted simultaneous sample extraction, removal of acidic and highly polar coextractables, and selective adsorption of the compounds of interest onto carbon (part II) and was readily

arrangement which simplified sample, solvent manipulations (Figure 2). Several sets of columns, each be loaded with a sample, the three solvents, and the enrichment processes allowed to proceed, by gravity solvent flow. The use of potassium silicate and silica gel ensures that the interfering lipid materials do not reach the carbon and permits the accurate estimate the amount of colored lipid material adsorbed by the potassium silicate/silica gel in those cases in which little or no accumulation is observed on column 2, consideration can be made of column 2 for another sample. Cesium silicate adsorbs acidic compounds more effectively than KS but is 50 times more costly. The operations of part I eliminate the need for extensive sample manipulations and are labor intensive. Such procedures which are employed in other methods include one or more of the following: (1) acidic or basic digestion of the sample, (2) liquid-liquid partitioning steps, (3) Soxhlet extraction, (4) gel permeation chromatography. The ability to perform enrichment procedures in a one-step, continuous manner can result in enhanced recovery and preparation to reduced analysis time. Furthermore, this procedure itself to the possibility of development into a multisample procedure (49).

Gas chromatography (GPC) was initially employed as an enrichment step preceding the analysis but often did not have the capacity for the sample required in these analyses. Furthermore, the use of GPC into the initial enrichment procedure required additional sample extraction and solvent volume to precede the GPC procedure.

In protecting the adsorptive capacity of the carbon, the silicate adsorbent has been demonstrated to remove acidic compounds which represent a major interference to determinations of PCDDs. The silicate adsorbents retain substances which have acidity constants of 10 and lower, including carboxylic acid compounds and sulfonamides. Additionally, hydroxy PCBs and hydroxydiphenyl compounds which can produce false-positive GC/MS results are effectively removed by the silicates (35).

Under the conditions of this enrichment procedure, the carbon will retain only a limited number of classes of compounds (50), including polyhalogenated planar aromatic compounds, to some extent PAHs with one or two rings, and strongly acidic compounds that are sequestered by the silicate adsorbent before reaching the carbon. The large majority of synthetic organic compounds which are commonly encountered as persistent contaminants are weakly adsorbed and readily desorbed from the carbon by the extraction solvent. Included among these are compounds which interfere in the determination of PCDDs, PCDFs, and non-ortho PCBs, DDE, PCBs, methoxy PCBs, polychlorinated PCBs (PCDPEs), and methoxy PCDPEs (35). The carbon also exhibits a very low affinity for the compounds which are not retained by the potassium silicate/silica gel combination.

In part II of the enrichment procedure (Figure 3) the sample is first passed through a strongly basic adsorbent, then through a strongly acidic adsorbent, 40% sulfuric acid silica gel (SA-SG), in the nonpolar solvent, and then subjected to chromatography on acid alumina. The use of the sample to cesium silicate in the nonpolar solvent hexane virtually assures the removal of

trace residues of acidic compounds. Use of cesium silicate which has been activated at 130 °C resulted in poor recoveries of hepta- and octachloro isomers. The adsorbent should simply be purged of solvent under a stream of nitrogen after preparation and not oven activated.

The sulfuric acid impregnated silica gel (40% w/w) has been demonstrated in this laboratory and elsewhere (51) to strongly retain or undergo chemical reactions with a number of classes of compounds. A series of polynuclear aromatic hydrocarbons (PAHs) possessing two to four condensed rings was found in this laboratory to be effectively retained by this adsorbent. The adsorbent is also undoubtedly very effective in removing numerous types of compounds by reactions of dehydration, acid-catalyzed condensations, and oxidation as demonstrated by the complete charring and polymerization of tissue extracts applied to this material. Colored bands of adsorbed materials are normally observed on the SA-SG adsorbent following sample application in part II of this procedure. The reactivity of this adsorbent toward PAHs is complementary to the activated-carbon adsorbent which strongly adsorbs certain PAHs which are subsequently recovered with the PCDDs, PCDFs, and non-ortho PCBs. Because polynuclear aromatic hydrocarbons will elute from alumina under the solvent conditions employed in the subsequent step involving alumina chromatography, it is important that PAHs be removed prior to this step. In some environmental samples, especially sediments, high concentrations of PAHs were frequently encountered.

The final step of the enrichment procedure, alumina chromatography, is designed primarily to separate PCDDs, PCDFs, and non-ortho PCBs from polychlorinated naphthalenes (PCNs), trace residuals of PCB isomers, and other polychlorinated aromatic compounds. In addition to PCDDs, PCDFs, and non-ortho PCBs the only classes of compounds which have been shown in this laboratory and elsewhere (46) to be recovered from the carbon are PCNs, polychlorinated biphenyls, and certain polychlorinated PAHs. The alumina chromatography removes the large majority of the 75 possible PCN isomers, but four to six penta- and hexachloronaphthalenes are partially recovered with the PCDDs, PCDFs, and non-ortho PCBs. Use of basic alumina (190 °C activated) requires higher concentrations of methylene chloride to recover PCDDs and PCDFs.

In-House and Extralaboratory Evaluations and Validation Studies. The following studies and evaluations were made: (a) determinations of the mean recoveries of a series of representative compounds of the three chemical groups at selected concentrations, (b) determinations of the coefficient of variation associated with each set of recovery data, (c) estimation of the lower limit of detection and determination of the various congener groups or individual components in a variety of sample types, (d) evaluation of the degrees of interference posed by seven series of polychlorinated aromatic compounds which represent the greatest threat of producing false-positive data, and (e) determination of the success rate for completed analyses of approximately 200 environmental samples.

Recovery Studies. Initial recovery studies were performed by using an abbreviated procedure which did not incorporate either the silica gel in part I or the alumina chromatography in part II. This procedure was highly effective for the determination of PCDDs, PCDFs, and non-ortho PCBs in biological materials. The major disadvantage of this abbreviated procedure appeared to be the inclusion of a large number of polychlorinated PAHs such as PCNs in the analyte. Nevertheless, an abbreviated procedure excluding alumina chromatography has been successfully used in the analyses of over 30 environmental samples. PCNs were the most significant cocontaminant observed but did not interfere in the deter-

Recoveries of Selected PCDDs and PCDFs in Salmon Oil from Abbreviated Procedure: Potassium Silicate, Alumina, Cesium Silicate, and Sulfuric Acid-Silica Gel^a

recoveries of selected compounds						
2,3,6,8- Cl ₄ -furan	2,3,7,8-Cl ₄ - dioxin	1,2,4,7,8-Cl ₅ - furan	1,2,3,4,7,8- Cl ₆ -furan	1,2,3,4,6,8,9- Cl ₇ -furan	OCDD	OCDF
109 [1]	115 [1]	115 [1]	113 [1]	117 [1]	86 [1]	79 [1]
recoveries of selected compounds						
2,3,7,8-Cl ₄ -furan 2,3,7,8-Cl ₄ - dioxin ^b	1,2,4,7,8-Cl ₅ - furan	1,2,4,6,7,9-Cl ₆ - furan	1,2,3,4,7,8-Cl ₆ - dioxin	1,2,3,4,6,8,9-Cl ₇ - furan	OCDD	OCDF
81 (9) [4]	70 (5) [4]	75 (5) [4]	82 (3) [4]	77 (5) [4]	87 (7) [4]	75 (5) [4]
102 (2) [4]	97 (3) [4]	84 (4) [4]	98 (2) [4]	87 (6) [4]	76 (3) [4]	74 (5) [4]
66 (2) [3]	80 (-) [2]	68 (3) [3]	76 (-) [2]	72 (8) [3]	66 (3) [3]	62 (14) [3]

were determined on a 12-m OV-17 WCOT glass column and electron capture detection (⁶³Ni) using helium at 50 cm/s and the temperature program: 190 °C for 2 min, then 4 °C/min to 240 °C and hold 15 min. Numbers in parentheses are coefficients of variation. Numbers in brackets are the number of replicate samples analyzed. ^b2,3,7,8-TCDD and 2,3,7,8-TCDF coeluted on the OV-17

Recoveries of Selected PCDDs and PCDFs from Spiked Samples of Homogenized Whole Fish Using the Enrichment Procedure

recoveries of selected compounds								
sample	2,3,6,8- Cl ₄ -PCDF	2,3,7,8- Cl ₄ -PCDF and PCDD	1,2,4,7,8- Cl ₅ -PCDF	1,2,4,6,7,9- Cl ₆ -PCDF	1,2,3,4,7,8- Cl ₆ -PCDD	1,2,3,4,6,7,9- Cl ₇ -PCDF	OCDD	OCDF
pike, carp and mud of PCDD and PCDF (100 ppb)	81 (1) [4]	92 (3) [4]	94 (3) [4]	98 (6) [4]	104 (4) [4]	95 (8) [4]	99 (22) [4]	91 (16) [4]

recoveries of selected compounds				
sample	[¹³ C]-2,3,7,8-TCDD	[³⁷ Cl]-2,3,7,8-TCDF	[³⁷ Cl]-1,2,7,8-TCDF	[³⁷ Cl]-OCDD
samples spiked at 25-50 ppb	82 ± 27 [49]	58 ± 16 [11]	75 ± 18 [10]	83 ± 30 [18]

recoveries of selected compounds ^a									
	Cl ₄ PCDFs	Cl ₅ PCDFs	Cl ₆ PCDFs	Cl ₇ PCDFs	OCDF	Cl ₅ PCDD	Cl ₆ PCDD	Cl ₇ PCDD	Cl ₄ biphenylene
spiked at 20 ppb	58 ± 10	64 ± 6	64 ± 7	63 ± 10	59	41	49	58	52
spiked at 100 ppb	52 ± 7	55 ± 4	53 ± 6	56 ± 4	52	84	60	51	59

of PCDDs and PCDFs. The recoveries of a series of PCDDs and PCDFs from spiked samples of salmon oil by the abbreviated procedures are given in Table I. The spiked fish samples containing up to 20 g of oil were carried out by GC/EC and showed very low levels of matrix components in the analytes (49). The incorporation of silica gel in part I and alumina in part II of the procedure, recoveries of a series of PCDDs from spiked whole fish samples were again determined (Table II). Recently, an independent evaluation of the procedure was carried out at the University of Wisconsin laboratory and included the determinations of recoveries of spiked fish of a mixture of fourteen tetra-, five penta-, three hepta-, and one octachlorodibenzo- and one tetrachlorobiphenylene (45). Mean and standard deviations of the recoveries are presented herein to support the effectiveness of the method for the con-

Only two sets of recovery determinations have been made for three representative non-ortho PCBs spiked at 100 ppb: 3,4,3',4'-tetrachloro (38 and 57%), 3,4,5,3',4'-pentachloro (43 and 47%), and 3,4,5,3',4',5'-hexachloro (54 and 59%).

The demonstration of the effectiveness of recovery of a large selection of PCDD and PCDF isomers, in particular those tetra-, penta-, and hexachloro isomers possessing the critical 2,3,7,8-chlorine substitution pattern, is especially important to defining the comprehensiveness and applicability of the method. The recoveries of all the isomers studied are generally comparable and no particular isomer or group of isomers appear to be selectively excluded by the enrichment procedure.

In addition to the recovery data derived from spiked samples as part of the validation studies, a substantial collection of recovery data was also generated for the four major components of the marker compounds which were added to each sample prior to the enrichment process. The marker compounds, [UL-¹³C]-2,3,7,8-TCDD, [UL-³⁷Cl]-OCDD, and a mixture of six [UL-³⁷Cl]-TCDFs including [³⁷Cl]-1,2,7,8- and [³⁷Cl]-2,3,7,8-TCDFs as the major components, were routinely incorporated into each sample at levels of 50, 50, 25, and 25 ppb, respectively. Although the range of recovery data values

Relative Recoveries of Tetrachlorodibenzo-*p*-dioxins from the Unabbreviated Enrichment Procedure^a

TCDD isomer	rel recovery	GC/MS peak no.	TCDD isomer	rel recovery
1368	1.20	8	1234, 1237, 1238, 1246, 1249	1.45
1379	1.27	9	1236, 1279	1.47
1378	1.57	10	1278, 1469	1.35
1369, 1247, 1248	1.47	11	1239	1.39
1268	2.13	12	1269	1.39
1478	1.30	13	1267	2.85
2378	1.00	14	1289	3.62

^a Approximately 2 ng of TCDDs was applied i.d. the enrichment procedure. Determination was made on a 60 m × 0.25 mm i.d. (J. & W. Inc.) capillary column under MID-EI mass spectrometric conditions: temperature, 200 °C for 1 min, then to 250 °C at 5 °C/min; He carrier gas.

marker compounds generally reflects the reduced GC/MS/DS quantitation of trace analytes using standard technique, the determinations of the marker compounds in these samples per- nearly a 3-year period provide a practical measure of the enrichment procedure and the analytical method (Table II). The average recoveries of the marker compounds over this extended period are consistently satisfactory with the exception of 2,3,7,8-TCDF which in early studies was observed to be uniformly low in comparison with those of the other compounds, most conspicuously with those of the [³⁷Cl]-TCDFs. A reexamination of the elution of 2,3,7,8-TCDF from alumina suggested that this step was the source of the problem; 2,3,7,8-TCDF eluted very early at the collection cutoff point. The addition of 5 mL of a 10% methanol solution to the collection volume increased the recovery of [³⁷Cl]-TCDF to levels comparable with those of the other compounds.

Determinations of background levels of PCDDs, PCDFs, and non-ortho PCBs were routinely made as part of the analytical protocol. Procedural blanks and samples of laboratory-reared fish, each spiked with the marker compounds, were incorporated at a frequency of about 10% in all sample sets. Analyses of these control samples were used to define the background level for sample sets and to estimate possible residue carry-over among samples. Of 14 procedural blanks, 1 produced a positive determination for OCDD at 1.6 ppb, 7 were positive for OCDD (1, 5, 7, and 11 ppb), 1 was positive for a 2,3,7,8-TCDF at 2 ppb, and 2 were positive for OCDF at 0.5 and 1.4 ppb. All of the 10 congener groups (total of 140 determinations) in these procedural blanks were negative and were below an average lower limit of detection of approximately 2 ppb. Of 11 analyses of samples of laboratory-reared carp, 7 produced positive determinations for OCDD (1, 1.5, 2, 3, 3, and 6 ppb), 1 was positive for OCDF at 4 ppb, 1 for a HCDF at 2 ppb, 3 for a HpCDF at 3 ppb, and 5 were positive for OCDF (1, 1, 2, 3, and 5 ppb). The remainder of the 110 determinations of PCDFs in these control fish were negative. The limit of detection was approximately 2 ppb. Non-ortho PCBs were not observed in these control samples, and the limit of detection for these compounds was approximately 5 ppb. In one series of control samples of laboratory-reared trout, a number of PCDF isomers were recovered at 10–20 ppb levels. These compounds were not detected as trace contaminants in the commercial fish samples used in the rearing.

Background levels of PCDDs, PCDFs, and non-ortho PCBs were negligible, especially for those isomers which followed the 2,3,7,8-substitution pattern. Octachlorodibenzo-*p*-dioxin, a common trace environmental

contaminant, being detected in more than 50% of the fish samples at levels significantly above those observed in the procedural blanks.

Although repeated analyses of procedural blanks between sample sets established a nondetectable level of carry-over between biological samples containing widely varying concentrations of PCDDs, PCDFs, and non-ortho PCBs, sample cross-contamination (from a carbon column) was observed to result from certain types of samples containing abnormally high levels of these contaminants. The samples causing cross-contamination were pond and river sediments and a sample of Aroclor 1260, all containing relatively high concentrations of PCDFs. Carry-over of PCDFs was readily demonstrated to result from reuse of the carbon columns and was observed in samples of fish which were processed on the same carbon column used for the highly contaminated samples. The degree of carry-over appeared to be on the order of 0.1%. In general, procedural blanks should be incorporated in sample sets at a frequency which will permit early detection of carry-over problems and should be included immediately following samples suspected of containing abnormally high concentrations of PCDDs, PCDFs, and non-ortho PCBs. Particularly in the case of sediment samples, high levels of other types of contaminants are routinely encountered, especially polynuclear aromatic hydrocarbons, and saturation of the carbon adsorbent with these substances may contribute to the problem of carry-over of PCDDs and PCDFs. In two cases of gross contamination of the carbon adsorbent, repeated washings of the column did not completely eliminate the problem, and the columns were replaced.

A satisfactory and reproducible level of recovery for 2,3,7,8-TCDD having been established, the recoveries of the other 21 TCDD isomers were examined. The mass chromatograms of a mixture of the 22 TCDD isomers (mixture provided by Dr. H. R. Buser, Swiss Federal Research Station, Wädenswil, Switzerland) before and after having been subjected to the enrichment procedure are presented in Figure 4. The relative recovery data, normalized to the recovery of 2,3,7,8-TCDD, are given in Table III. These data, although not rigorously demonstrative of satisfactory recoveries for each of the other 21 isomers, do establish that most of these isomers were effectively recovered by the procedure. In fact, in this experiment all other isomers or groups of isomers were apparently recovered more efficiently than was 2,3,7,8-TCDD. The abnormally high calculated recoveries of the 1,2,6,8-, 1,2,6,7-, and 1,2,8,9-TCDDs, each a minor component of the mixture, are attributed to the disproportionate influence of variations in instrumental sensitivity on analyte response near the limit of quantitation.

Probably the most useful piece of information derived from an examination of the determinations of the marker compounds in the hundreds of samples was the fact that the success rate for analyzability of the samples was better than 99% and that the minimum level of detection consistent

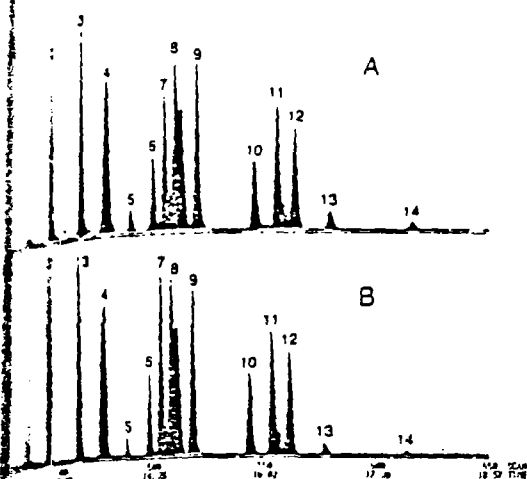


Fig. 3. MS-MID electron impact ion chromatograms of 2,3,7,8-TCDD: (A) following application of enrichment procedure; (B) without enrichment.

of 1–10 ppt with an average value of less than 1 ppt. Samples and controls were routinely spiked at the 10 ppt level with each of the marker compounds. In all cases, the positive and uniform responses of the marker compounds in each of the analytes, GC/MS, PCDDs and PCDFs at low parts-per-trillion levels were readily attainable. Estimates of the lower limit of detection (LOD) for TCDDs, TCDFs, and OCDD were made from the observed signal-to-noise value for the marker compounds (internal standards) to the values corresponding to a signal-to-noise value of 3. LOD require comparisons of the noise levels in each of each group of compounds and appropriate use of the internal standards.

Determination of PCDDs, PCDFs, and non-ortho PCBs was increasingly difficult at levels approaching the limit of detection, particularly to increased variations in the values of the isotopic components of the molecular ions. Determination of the correct isotopic abundance ratios of molecular ions in determinations of PCDDs and PCDFs at low parts-per-trillion levels was usually the most difficult to meet once sufficient instrumental sensitivity was attained. Nevertheless, over 50 separate confirmations were made of PCDD and PCDF residues present at 1 ppt. The criteria for the confirmation of any PCDD, PCDF, or non-ortho PCB of unspecified substitution were: (1) signal-to-noise ratio of ≥ 3 ; (2) correct molecular mass; (3) coincidental maxima of three or more scans of individual members of the molecular ion cluster; and (4) chlorine isotope ratios within 10% of the expected values for three to six members of the molecular ion cluster.

For routine monitoring of the fragment ions of 2,3,7,8-TCDD, the characteristic loss of COCl from PCDDs and PCDFs was investigated and determined to be marginal for detection at part-per-trillion levels due to the relatively low abundance of these ions. The criteria for confirmation of 2,3,7,8-TCDD also include a requirement of demonstrating a unique relative retention time within 2–4 parts per thousand. For example, 2,3,7,8-TCDD is sufficiently resolved from other TCDD isomers on both a Silar 10C (31) and a DB-5 (32) capillary column to enable easy determination of acceptable limits for the variation in retention time of this isomer relative to that of the isotopic components of 2,3,7,8-TCDD. The retention time of 2,3,7,8-TCDD on the DB-5 column was also found to be well resolved from the 1,2,3,7- and 1,2,3,8-TCDD isomers, indicating that their presence could be observed

but would not produce a false-positive determination. The variation in the retention time of 2,3,7,8-TCDD relative to that of [^{13}C]-2,3,7,8-TCDD on the DB-5 column was observed in numerous analyses of standard mixtures of the two compounds and found to be within 2 parts in 1000. All confirmations of 2,3,7,8-TCDD in samples analyzed by this procedure met this requirement and were often repeated on a Silar 10C column. Samples of particular importance were independently analyzed by other laboratories using complementary techniques such as high-resolution mass spectrometry or atmospheric-pressure chemical ionization mass spectrometry (53). Over 20 samples analyzed in this laboratory for PCDDs and PCDFs were subjected to independent analyses in other laboratories, including those of H. R. Buser (Switzerland Federal Research Station, Wädenswil, Switzerland) (54), Ronald Mitchum (National Center for Toxicological Research, Jefferson, AR) (55), Michael Gross (University of Nebraska, Lincoln, NB) (55), Robert Harless (USEPA, Research Triangle Park, NC), David Firestone (U.S. Food and Drug Administration, Division of Chemistry and Physics, Washington, DC) (56), John Ryan (Health and Welfare Canada, Food Division, Ottawa, Canada) (57), Patrick O'Keefe (New York State Department of Health, Albany, NY) (26), and Christopher Rappe (University of Umea, Umea, Sweden) (Table IV). The Columbia laboratory also participated in three interlaboratory studies of the effectiveness of different methods for the determination of 2,3,7,8-TCDD in fish. The agreement in both identification and quantitation between the results from this laboratory and those of the other laboratories was consistently good, and no false-positive results were indicated in any of the determinations made with this procedure (Table IV). In the majority of interlaboratory studies, the comparisons involved only determinations of 2,3,7,8-TCDD.

Evaluation of Potential for Interference from Cocontaminants. Determinations of PCDDs, PCDFs, and non-ortho PCBs in environmental samples at levels below 1 ppt are particularly susceptible to interferences and possible false-positive results as a consequence of the likely occurrence of a large variety of polychlorinated aromatic cocontaminants and because full-scan mass spectrometric analyses are usually unattainable. More than a dozen families of such compounds are recognized as potential interferences in these types of analyses (35, 58), including DDE and DDT and polychlorinated members of the following compounds: biphenyl (59), methoxybiphenyls (60), hydroxybiphenyls, diphenyl ether (61), methoxydiphenyl ethers, hydroxydiphenyl ethers (62), benzyl phenyl ether (63), naphthalene, biphenylene, phenylbenzoquinone (64), xanthene, and bis(phenoxymethane) (65). Most of these families of compounds have the potential to interfere with and produce false-positive results in determinations of PCDDs and PCDFs even in HRMS (35). The problem of interferences in determinations of PCDDs and PCDFs has been rigorously addressed experimentally in only a few publications (66), and in these was limited to a small proportion of the numerous families of potential interferences. Routinely, conclusions in regard to the potential for interferences in analytical procedures for PCDDs and PCDFs are made by inference from observations of the effectiveness of separation of comparable amounts of these interfering compounds from PCDDs and PCDFs, often with a relatively small number of isomers of these two families. For example, alumina has been shown to effectively separate PCBs from certain PCDD isomers (67). A more appropriate evaluation should include a large number of isomers of and a large excess concentration (10^4 – 10^6) of the potential interference relative to that of PCDDs or PCDFs.

As part of the validation of this procedure an evaluation was made of the degrees of interferences produced by seven

Independent Laboratories

and. ¹Samples were not analyzed due to large amounts of materials in analyte. ²Sample was lost. ³Reference 50. ⁴Reference 51. ⁵HRGC/MS APL. ⁶HRGC/HRMS EI.

also recovers isomers of polychlorinated
A large number of isomers of polychlorinated
were identified in this laboratory in a sample

The susceptibility to interferences of these types of analyses is demonstrated by the results of an interlaboratory study conducted by the USFDA (56) of the effectiveness of six different enrichment procedures (for 2,3,7,8-TCDD) performed by six independent laboratories (see Table IV). The enriched samples were all returned to the USFDA laboratory for rigorous analysis. Of the seven sets of analytical results only two.

Precision of Quantitation Using Internal Standards in GC/MS and GC/EC Analyses Before and After the Enrichment Procedure

	before enrichment procedure			after enrichment procedure		
	mean response by GC/MS ^b	% std dev by GC/MS ^b	% std dev by GC/EC ^c	% std dev by GC/MS ^b	% rel recovery by GC/MS ^b	% rel recovery by GC/EC ^c
	1.39	6	8	12	97	109
	0.54	17	5	8	96	113
	1.40	7	2	14	97	128
	0.05		2		160	129
	1.05	7		5	85	
	0.92	15	4	19	140	127
	1.36	19	10	9	80	107
	5.63	10	2	15	109	126
	1.60	9	4	16	113	150
	1.29	9	5	17	133	137
	1.18	5	5	17	143	150
	0.80	8	7	15	153	141
	0.97	11	4	20	135	157
	0.42	12	8	26	195	159
	0.31	26	7	36	177	114
	0.44	27	7	30	164	114
	0.18	5		5	117	
	0.88	10		13	103	
	0.97	6		14	78	
	1.00				100	
	0.66	18		18	115	
		11.9	5.1	16.3		
		9.8	4.9	14.1		

OCDD = PCDD. ^b [¹³C]-2,3,7,8-TCDD used as reference compound. ^c 2,3,7,8-TCDF used as reference compound.

that generated by this laboratory, were judged to be compromised by the presence of significant levels of interfering substances. In fact, the presence of amounts of superfluous substances in a number of samples prevented the determination of TCDD in 5 samples and apparently produced positive interferences in 3 fortified samples, as indicated by quantitative analyses which were significantly greater than the levels of

Enrichment Procedures. Quantitations of 2,3,7,8-TCDD, 2,3,7,8-TCDF, and OCDD are made directly by comparison of the integrated responses of the native compounds with those of the isotopically enriched marker compounds. This is made by analysis of known amounts of the marker compound and an authentic quantitative amount of the native material under those GC/MS conditions used in analysis of samples.

In the first 2 years of use of this procedure, quantitations of other PCDDs, PCDFs, and non-ortho PCBs were made by the external standard technique using mixtures of 12 compounds. Toward the latter half of 1982, quantitations of these compounds were performed using the major isotopic marker compounds as internal standards for all congeners. Usually [³⁷Cl]-OCDD was used for quantitation of OCDD and OCDF, and [¹³C]-TCDD and [³⁷Cl]-2,3,7,8-TCDF were used for quantitation of all other PCDDs, PCDFs, and non-ortho PCBs. Relative response factors for the various congener groups were determined by GC/MS analyses of mixtures of isotopic marker compounds and a series of 20 synthesized PCDDs, PCDFs, and non-ortho PCB isomers.

An attempt was made to determine the suitability, in terms of accuracy and precision, of quantitations of all congener groups using the internal standards (isotopic marker compounds). The experiment involved GC/MS-MIM and GC/EC analyses (5 replicates each) of a mixture of 17 native PCDDs and the 5 isotopically enriched marker com-

pounds. This mixture was subsequently subjected to the enrichment procedure (5 replicates) and analyzed again by GC/MS-MIM and by GC/EC. The mean and standard deviations of the integrated responses of all compounds relative to that of [¹³C]-2,3,7,8-TCDD were determined by GC/MS, and 2,3,7,8-TCDF was used as the internal standard in GC/EC analyses (Table V). The level of variation as measured by standard deviation for GC/MS quantitations using the internal standard was twice that determined for the GC/EC analyses. The data indicate that GC/MS quantitations using TCDD or TCDF as an internal standard were significantly more precise for tetrachloro through heptachloro congeners than for OCDD and OCDF. In contrast, no such disproportionate trends in precision were observed in the GC/EC analyses. The large variations associated with OCDD and OCDF are believed to be in part a consequence of GC/MS instrumental problems which were being experienced at the time and not necessarily characteristic of these types of analyses. Analyses of the mixture following application of the enrichment procedure show that the mean standard deviation is increased but comparable to instrumental variation. Nevertheless, the results indicate an acceptable level of precision for GC/MS quantitations of Cl₄ through Cl₇ congeners using a TCDD or TCDF as an internal standard in samples subjected to the enrichment procedure.

Determinations of PCDDs, PCDFs, and non-ortho PCBs were routinely carried out in the electron impact GC/MS mode. The GC/MS-EI technique, in contrast to negative ion chemical ionization analysis, exhibits comparable sensitivity for the broad range of congeners and permits identification and quantitation of all components in a single analysis. Negative ion chemical ionization GC/MS (GC/MS-NICI) has been observed in this laboratory and elsewhere (70) to exhibit a markedly enhanced sensitivity to PCDFs relative to PCDDs and, generally, to the higher relative to the lower chlorinated congeners of both groups. The ability to determine tetrachlorodioxins and tetrachlorobiphenyls in particular suffers

...NICI, and consequently this technique is un-
complete determination of PCDDs, PCDFs, and
at part-per-trillion levels. On the other hand,
is much less sensitive to background (especially
hydrocarbons) or cocontaminant substances
yielded more easily interpretable data.

...of Extraction. The implicit assumption in
using the internal standards incorporated at the
of the procedure is that the behavior of an iso-
merized compound will be identical with that of the
parent compound present in sample. This assumption is
questioned for all enrichment processes except that
of residues from the sample matrix. The
of extractability of bioincorporated contami-
nants in biological samples or sorbed residues from soils
and products is particularly important in studies
of PCDDs. Studies of the biochemistry of
and related compounds in mammalian systems
have established that these compounds exhibit high
binding affinities for a hepatic cytosol protein; con-
servation of some PCDDs, PCDFs, and non-ortho
biological samples may involve more than the
of these residues from solution in fatty deposits.
have been reported of the efficiency of extract of
of PCDDs, PCDFs, or non-ortho PCBs. On the
comparisons of the results of interlaboratory
Table IV) involving a wide variety of extraction
and for identical samples of fish containing
of 2,3,7,8-TCDD have provided a reasonable
of extractability of this substance from fish tissue.
of these studies suggest that the neutral column
employed in this procedure is essentially equivalent
to extractions involving complete digestion of the
concentrated aqueous base or acid. Such digestions
of to denature and hydrolyze all proteins and to
of intact TCDD residues. Referring to
laboratory no. 1 in the USFDA study employed
of concentrated HCl; in the H&WC/USFDA
laboratory no. 3 employed digestion with KOH, and
laboratory no. 7 employed digestion with HCl. Assuming that
TCDD is as strongly bound in these samples of fish
as any other PCDD, PCDF, or non-ortho PCB, the
extraction procedure is expected to effectively recover
residues of these compounds. The effectiveness of
extraction could be species dependent and cannot
be extrapolated to other animal systems without similar studies.
Our rationale for addition of the internal
standards to the samples at the beginning of the extraction
was that before homogenization and mixing of the
sample, the internal standards could not be easily at-
tached to the internal standards. Consequently, losses in the homo-
genization and drying step are not included in the internal
standardization procedure.

...adsorptive interaction of PCDDs, PCDFs, and
PCBs with carbonaceous materials has been studied
extensively, and studies of fly ash containing these com-
pounds have demonstrated that exhaustive extraction pro-
cedures are required (72). Consequently, a study was un-
dertaken in this laboratory to determine the relative effi-
ciencies of methods of extraction of these compounds from
sediment samples (73). The neutral column
extraction procedure was compared with a procedure (72)
which had been demonstrated to be effective for the recovery
of residues from fly ash. Although the results of the com-
parisons were highly variable and no unambiguous
conclusions regarding the relative efficiencies of the two procedures could
be drawn, neither of the procedures was uniformly superior

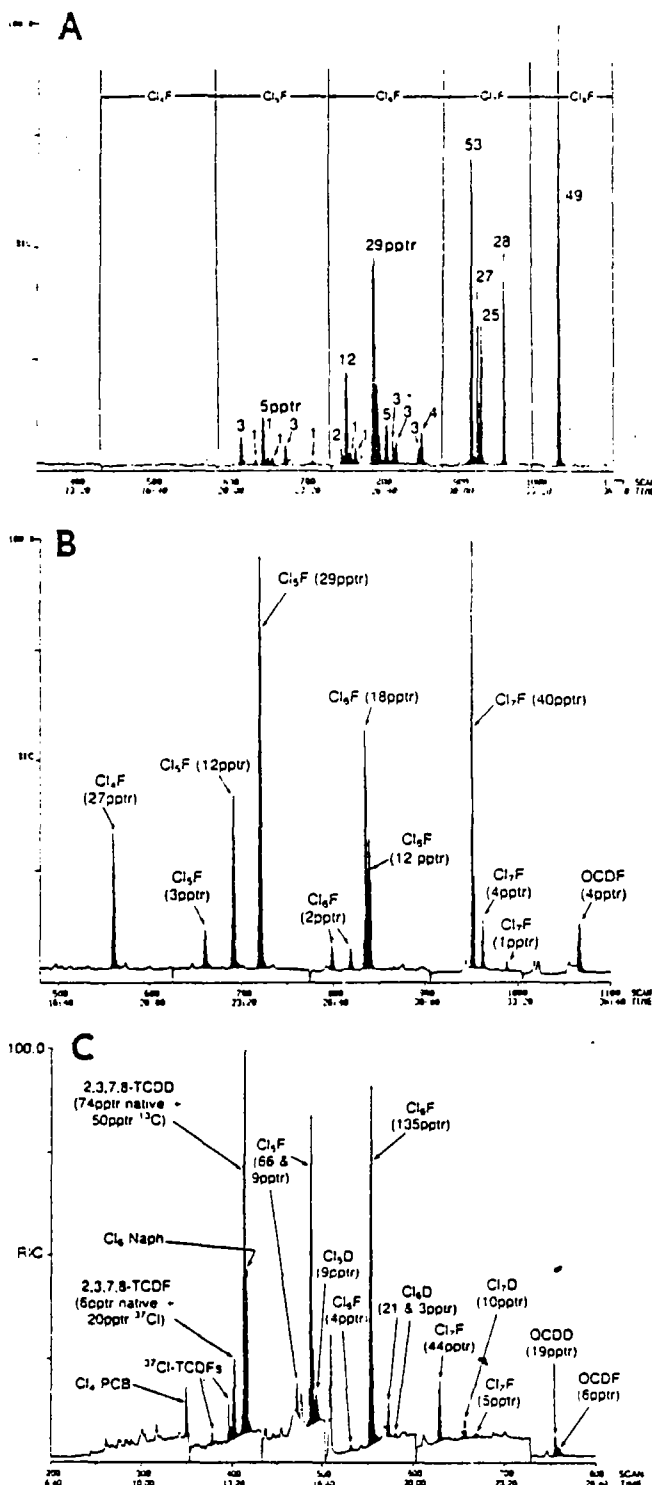


Figure 5. Representative analyses of environmental samples: (A) GC/NICI-MS-MID PCB contaminated soil from Fountain City, WI; (B) GC/NICI-MS-MID fish sample (carp) from Saginaw Bay at Bay City, MI; (C) GC/EI-MS-MID fish sample (carp) from the Niagara River at Ft. Niagara, NY.

to the other and appear to be roughly comparable in effectiveness. More definitive results are required from such studies before the efficacy of the column extraction procedure in analyses of soil and sediment samples can be established.

Applications to the Analyses of Environmental Samples. The procedure has been applied to the determination of PCDDs, PCDFs, and non-ortho PCBs in a wide range of sample types, primarily fresh-water fishes. The sample types which have been analyzed include about 12 species of fresh water fish (55, 68) and three species of salt water fish (both whole body and fillet): snapping turtle fat (54), white body

approximately five species of fresh water mussels, muscle and eggs of three species of birds, Baltic aquatic macroinvertebrates, commercial fish and terrestrial soils (73), soot from an office involving PCBs and polychlorinated benzenes (26), motor 1260, and failed transformer fluid from the. The large majority of these samples were on the five Great Lakes and selected tributaries of the Mississippi, Hudson, and Sacramento Rivers, and board rivers and estuaries, and the Housatonic Massachusetts and Connecticut known to be contaminated with a wide range of persistent synthetic chemicals including organochlorine pesticides, and industrial wastes. A number of samples analyzed was approximately including over 50 control and procedural blank. Essentially all of the 250 analyses were judged to be according to the following criteria: (1) All marker were detected in the analyte. (2) An acceptable detection (usually less than 5 ppb) was achieved. (3) GC/MS properties of analyte components including PCDDs, PCDFs, and non-ortho PCBs did not show significant interferences. (4) The criteria for the detection of PCDDs, PCDFs, and non-ortho PCBs were

multiple ion mass chromatograms of soil samples are presented in Figure 5. These GC/MS analyses of PCDDs, PCDFs, and non-ortho PCBs in these types of samples serve to exemplify the procedure for such analyses. The GC/MS analysis was uncluttered by extraneous components, and the data was routinely straightforward.

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Activity of Negative Ion Chemical Ionization Mass Spectrometry for Benzo[a]pyrene

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Chromatography/negative ion chemical ionization mass spectrometry (GC/NICIMS) was used as a selective and sensitive technique for the detection of benzo[a]pyrene (BaP). Under optimized conditions, the molecular anion, M^- , of BaP was more than 3 orders of magnitude more abundant than the isomer benzo[e]pyrene (BeP) using methane as the reagent gas. Quantities of BaP as low as 1 pg can be detected in the selected ion monitoring mode and the response vs. concentration was linear over a range of 3 orders of magnitude. The absolute sensitivity and the selectivity of detection were found to depend on the pressure and temperature in the ion source of the mass spectrometer. GC/NICIMS was used for the quantitative determination of BaP, BeP, and benzo[ghi]perylene in a sample of petroleum crude oil as part of the process of certifying the oil as a Standard Reference Material.

Negative ion chemical ionization (NICI) mass spectra can be obtained from certain organic compounds by resonance transfer of thermal electrons if the molecules have positive electron affinities, and if the internal energy of the molecular anion is less than the electron affinity of the neutral species. The major species formed is the molecular anion, M^- , which yields relatively large ion currents and little fragmentation. The selectivity of NICI over electron impact ionization is well established and this feature has permitted wide applications over the past few years in the analysis of compounds such as polychlorinated biphenyls (1), pesticides (1, 4, 5), and nitrated polycyclic aromatic hydrocarbons (6). Iida and Dashima (7) recently used the methane negative ion chemical ionization mass spectrometry for the analysis of polycyclic aromatic hydrocarbons (PAH). Oehme (8) used NICI to determine PAH in air particulate matter using NICI. He used a mixture of methane and nitrous oxide as the reagent gas for negative ionization by electron capture and ion/molecule reactions and was able to differentiate isomeric PAH by the relative abundances of various species formed. Cooper, and Cooks (9) used negative ion chemical ionization mass spectrometry as a highly sensitive means for determining polycyclic aromatic hydrocarbons in a solvent refined coal. This paper describes the use of NICI mass spectrometry as a sensitive and selective technique for the quantitative determination of

benzo[a]pyrene (BaP) in a sample of petroleum crude oil which is being certified as a Standard Reference Material (SRM). During the course of preliminary studies we have confirmed the large degree of selectivity for the detection of BaP over benzo[e]pyrene (BeP) noted by others (7, 8). We have observed the molecular anion of BaP to be more than 1000 times more abundant than that of BeP under selected source conditions in the NICI mode using methane as the reagent gas. Our observations, reported here, show that the ion source pressure and temperature play an important role in the selectivity of detection for BaP. We have also observed excellent absolute sensitivity for the detection of BaP and are able to detect quantities as low as 1 pg in the selected ion monitoring mode.

EXPERIMENTAL SECTION

Negative ion chemical ionization mass spectra were recorded on a Hewlett-Packard 5985B quadrupole GC/MS system (Hewlett-Packard Co., Palo Alto, CA) with a dual EI/CI ion source and electronics capable of detecting negative ions. Chromatographic separations were carried out on a 30 m \times 0.25 mm i.d. fused silica capillary column coated with a 0.25- μ m film of a nonpolar liquid phase. Samples were injected in either the split or splitless modes with an injection port temperature of 300 °C and the column temperature was programmed from 200 to 300 °C at a rate of 4 °C/min. The column was interfaced directly to the ion source by inserting it through a 30 cm length of 0.16 cm o.d. stainless steel tubing. The stainless steel tubing also served as a conduit for introduction of the methane reagent gas (Matheson Ultra High Purity 99.97%) which was brought in coaxially with the capillary column. The pressure in the ion source was adjusted by varying the methane flow into the source via a flow controller. An ionization gauge, which was mounted approximately 15 cm from the source, was used to monitor the ion source manifold pressure. The pressure in the ion source itself was measured with a thermocouple gauge. Spectra were recorded under conditions optimized empirically for the detection of BaP. The ion source was normally operated at 200 °C with a filament emission current of 300 μ A and a primary electron beam energy of 60 eV. The mass spectrometer was calibrated in the NICI mode using ions at m/z 414, 452, and 633 from perfluorotributylamine and ions at m/z 233 and 235 from rhenium oxide generated by the filament. The ReO_3^- isotopes provide a good source of ions at low mass for tuning the mass spectrometer in the negative ion mode.

The PAH were obtained commercially: BaP (Community Bureau of Reference, BCR, Brussels, Belgium); BaP- d_{12} 98.6 atom % D (MSD Isotopes, St. Louis, MO); and BeP (Pfaltz and Bauer, Inc., Stamford, CT). The standards were analytical grade or higher and were used without further purification. Methylene chloride solutions of the PAH were prepared gravimetrically. The Wilmington crude oil sample was obtained from the Department of Energy and is one of the oils being stored in the EPA Repository

ATTACHMENT 3

PROCEDURES FOR FISH SAMPLE PREPERATION

SPECIFICS FOR THE CRAB ORCHARD PROGRAM

Only the edible portion of the fish will be analyzed for PCBs. The edible portion as defined by the FDA for the fish species collected from the Crab Orchard site are:

Carp	Fillet Skin On
Channel Cat	Fillet Skin Off
Bullhead	Fillet Skin Off
Largemouth Bass	Fillet Skin On

In addition, five fish of each species will be composited into one sample. Equal portions of the ground fillets will be mixed into one. The remaining portions will be stored frozen.

Prior to processing, each fish will be weighed and its length measured.

SAMPLES

This section gives general guides for preparing and compositing routine samples. It does not provide for handling the unusual sample. Because complete background information on samples is ordinarily unknown, and since residue analysts are usually unaware of what residues are present or of how they were incurred, *no sample should be assumed to be routine.*

A thorough visual examination of the gross sample should always be made before any preparation or compositing is begun. This should be on a sub by sub basis if sample is received in subsample form. A key to proper sample analysis can often be found by observation of the general appearance and odor of the product. Presence of soil, dust, wax, powder or stains; and foreign or off odors should be noted and recorded. When appearance or odor of the sample (or any of its subs) is unusual, the applicability of instructions in 141 and 142 should be carefully weighed before preparation and compositing are begun.

SAMPLE PREPARATION

Where samples are analyzed to determine whether they are in compliance with the Federal Food, Drug, and Cosmetic Act, they must be prepared for analysis according to preparation specified in the Regulations¹ or in Administrative guidelines which have been established for the residue on the commodity. The various ways to prepare raw agricultural and processed foods are given in 141.1 and 141.2 as an aid to residue analysts in proper choice of how to handle residue samples.

The portion of sample taken for analysis must be representative of the gross laboratory sample. It must be carefully handled to prevent loss of residue by volatilization and to prevent concentration of residue through physical separation of product during preparation. Meaningful residue data can only be obtained when integrity of sample is preserved. Haphazard preparation results in data that is useless and often misleading.

¹ Federal Food, Drug, and Cosmetic Act Regulations. Published in the Code of Federal Regulations, 40 CFR, part 180 - Protection of Environment, and 21 CFR, part 121, and 21 CFR, part 122 - Food and Drugs.

141.1 Raw Agricultural Commodities. Raw agricultural commodities include, among other things: fresh fruits, whether or not they have been washed, colored or otherwise treated in their unpeeled natural form; vegetables in their raw or natural state, whether or not they have been stripped of their outer leaves, waxed, prepared into fresh green salads, etc.; grains, nuts, eggs, raw milk, meats, and similar agricultural produce.

There are different ways required for preparing raw agricultural commodities for residue analysis. The various preparations are described as follows:

- (1) **Whole Raw Agricultural Commodity.** — Most tolerances have been established on the product in its raw or natural state as shipped in interstate commerce. The whole raw agricultural product is prepared for analysis as in 141.12a.
- (2) **Whole Basis According to Regulation 40 CFR 180.1(j).** — This regulation directs which portion of the commodity is to be discarded and which portion is to be taken for analysis, and is in accordance with how most tolerances were established on these products. Commodities for which preparation has been specified are listed in 141.12b, along with their regulation reference. This preparation is considered "whole basis" preparation for these commodities only.
- (3) **Whole Basis According to Specific Tolerance Regulations (40 CFR 180 Subpart C).** — Special preparation for certain commodities is directed by the individual tolerance regulation. When samples are selectively collected for a specific residue, consult the tolerance regulation to determine if the portion of the commodity to be analyzed is specified.
- (4) **Edible Portion.** — Inedible portions of the product are discarded and edible portion only is analyzed. The edible portion preparation for several commodities is listed in 141.12c. Analysts should use discretion in determining the inedible portion of products not listed in that section.

Analytical report must give full description of product as received for analysis and must clearly state the exact portion of food used for analysis.

141.11 Guide to Determining How to Prepare Raw Agricultural Commodities. The criteria for using the various preparation procedures for raw agricultural commodities (141.1) are listed here to aid the residue analyst in determining how to prepare samples for analysis. Determine, from any information available, the type of sample and reasons for analysis. Use the preparation procedure for that type sample.

GENERAL INFORMATION
Section 141.11

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Sample
Type

Criteria

Procedure

I-R

Meets *ALL* of the following criteria:

(a) Collected for multi residue determination.

(b) No background information or background information does not indicate likelihood of contamination by specific pesticide or industrial chemical.

(OBJECTIVE SAMPLES).

(c) Commodity has at least one residue tolerance established and that residue is determined by methodology to be used.

Consult 141.12b and, if product is listed there, prepare as directed; if not listed, prepare the whole raw agricultural commodity as in 141.12a

II-R

Meets *EITHER* of the following criteria:

(a) Selectively collected for a particular residue for which a tolerance is established.

(b) Analysis of a type I-R sample reveals a significant residue which has an established tolerance on the product.

Consult the specific tolerance regulation listed in 40 CFR 180 Subpart C or 21 CFR 122 for preparation that may be required by regulation.

III-R

Meets *ANY* of the following criteria: (a) No tolerances have been established for any residue on the commodity or the chemicals with established tolerances on the commodity are not determined by methodology used.

(b) Selectively collected for a particular residue for which no tolerance has been established on that particular commodity (e.g. endrin in melons).

(c) Collected from an area where a known residue problem exists for a chemical for which no tolerance has been established on the particular commodity.

(d) Analysis of a sample prepared as in 141.12a or in 141.12b ("whole basis") reveals significant quantity of a residue for which no tolerance has been established on the particular commodity.

Prepare sample according to the edible portion guide 141.12c.

141.12 Preparation of Raw Agricultural Commodities

141.12a Whole Raw Agricultural Commodity. Remove obviously decomposed leaves, berries, etc. Prepare the whole raw agricultural product. See 141.1(1).

141.12b Whole Raw Agricultural Commodity with Preparation Specified in 40 CFR 180.1(j). Prepare commodities listed in table below according to preparation in column b. See 141.1(2). Preparation given in Editors' Notes is in keeping with current policy.

141.12c Edible Portion. Prepare commodities listed in table below according to preparation in column c. See 141.1(4).

Commodity	Preparation	
	b Specified in 40 CFR 180.1(j)	c Edible portion
Bananas	Remove and discard crown tissue and stalk. 40 CFR 180.1(j)(1) (Editors' Note: Several specific tolerance regulations establish separate level for pesticide in pulp.)	Remove and discard peel; examine pulp only.
Corn, sweet	(Editors' Note: Some tolerance regulations specify portion for analysis as "kernels plus cob; husks removed.")	Remove and discard husks and cob; examine kernels.
Crabs, hard shell	(Editors' Note: Use edible portion guide.)	Examine a homogeneous mixture of meat and fatty materials isolated as described below: Heat crab in boiling water or place in autoclave under flowing steam for one minute if previously frozen, or five minutes if sample has been merely chilled and is possibly still alive. Remove claws and other appendages and pick out meat. Remove back shell. Clean out and discard viscera and gills (easily remove by hand).

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Commodity

Preparation

^b
Specified in 40 CFR 180.1(j)

^c
Edible portion

Include in the edible portion fatty material (yellowish colored) from inside tips of the back shell and any fatty material (yellowish colored) adhering to meat. Break crab in half and remove meat from body cavity excluding shell and other obviously extraneous materials.

Crab, soft shell (Editors' Note: Use edible portion guide.)

Examine entire crab.

Eggs (Editors' Note: Use edible portion guide.)

Discard shells; examine combined yolks and whites.

Fish (raw) (Editors' Note: Use edible portion guide.)

Remove and discard heads, scales, tails, fins, guts and inedible bones; do not remove skin; fillet to obtain all flesh and skin from head to tail and from top of back to belly on both sides. Where extremely large whole fish are to be analyzed and filleting is impractical, 3 cross-sectional slices from each fish may be taken and combined.

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Commodity

Preparation

^b
Specified in 40 CFR 180.1(j)

^c
Edible portion

Clean, scale and eviscerate fish. Take 1" thick slices, one from behind the pectoral fins, one from half way between first slice and the vent, and one from behind the vent. Remove bones from each slice before combining.

Rule of edibility supersedes these directions; e.g., catfish skin (inedible) is discarded.

Fruits (general comment)

Remove and discard stems.

Fruits, stone

Remove and discard stones or pits.

Garlic bulbs

Remove and discard roots, stems and outer sheaths (or husks); examine garlic cloves only. 40 CFR 180.1(j)(5)

Same as preparation in 40 CFR 180.1(j)(5)

Mangoes

Remove and discard rind and stone.

Melons

Remove and discard stems. 40 CFR 180.1(j)(4)

Remove and discard rind, stem and seeds; examine edible portion.

FORM FD 2905a (11/76)

TRANSMITTAL NO.

77-1 (03/01/77)

Commodity

Preparation

	^b Specified in 40 CFR 180.1(j)	^c Edible portion
Nuts	Remove and discard shells. 40 CFR 180.1(j)(2)	Same as preparation in in 40 CFR 180.1(j)(2)
Oysters, Clams (raw)	(Editors Note: Use edible portion guide.)	Examine a homogeneous mixture of meats and liquor.
Peanuts	(Editors Note: Use edible portion guide.)	Remove and discard shells.
Pineapple	Remove and discard crowns (leaves at the top of the fruit). 40 CFR 180.1(j)(7)	Remove and discard crown and flowers (outer protective petals); examine edible portion only.
Pumpkins		Remove and discard rind, stem and seeds; examine edible portion only.
Root crops (general comment)	(Editors Note: Use edible portion guide.)	Rinse lightly to remove adhering soil.
Root vegetables including tops or with tops	Examine the roots and tops separately. Neither the pesticide residues on the roots nor on the tops shall exceed the tolerance level, except that in the case of carrots the tops shall be removed and discarded before analyzing roots for pesticide residues. 40 CFR 180.1(j)(6)	Same as preparation in 40 CFR 180.1(j)(6)
Shrimp (raw), crawfish and similar shellfish	(Editors Note: Use edible portion guide.)	Remove and discard heads, tails and shells; examine edible meat only.

FORM FD 290a (11/74)

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GENERAL INFORMATION
Section 141.12

Commodity

Preparation

Strawberries

^b
Specified in 40 CFR 180.1(j)

Remove and discard caps
(hulls).
40 CFR 180.1(j)(3).

^c
Edible portion

Same as
preparation in
40 CFR
180.1(j)(3).

FORM FD 2905a (11/74)

TRANSMITTAL NO.

77-1 (03/01/77)

141.22 Preparation of Processed Foods

141.22a "As is" Product. Prepare the "as is" food (including concentrates, dehydrated foods, etc.) as received or as when introduced into interstate commerce.

141.22b Certain Commodities with Specified Preparation. Prepare as directed below:

Canned foods

Examine a homogeneous mixture of can contents; except, drain and discard brine and remove pits and stones.

Cheese

Do not remove or discard natural cheese rind. Do remove and discard waxed or oiled rings. Grind, dice, shred or blend cheese. See 142.22b.

Citrus pulp, Milk,
Tomato pomace

Examine produce as received or as when introduced into interstate commerce.

Fish, breaded, raw
or cooked

Do not remove breading. Fillet as necessary (as described in 141.12 "fish (raw)") to remove bones and/or tails.

Fish, canned in
brine or water

Drain and discard liquid, examine remainder.

Fish, canned in
oil, broth or sauce

Examine a homogeneous mixture of can contents.

Fish, frozen

Thaw, drain and discard drainings. Fillet - use entire piece. Whole fish - proceed as in 141.12 "fish (raw)."

Fish, smoked

Proceed as in 141.12 "fish (raw)."

Frog legs

Discard bones; examine edible meat only.

Oysters and Clams,
canned or frozen

Examine a homogeneous mixture of meats and liquor.

Shrimp and similar
shellfish, breaded

Examine as received.

Shrimp and similar
shellfish, canned
in brine

Drain and discard brine; examine edible meat.

Shrimp and similar
shellfish, frozen

Thaw, drain and discard drainings. Remove and discard heads, tails and shells; examine edible meat only.

FORM FD 202a (11/76)

141.2 Processed Foods. Processed foods include foods that have been processed, fabricated, or manufactured by cooking, freezing, dehydrating or milling.

The various ways of preparing processed foods for analysis are as follows:

(1) "As is" Product. The food or feed as shipped in interstate commerce is prepared for analysis. Concentrates, dehydrated foods, etc. are analyzed "as is". Do not reconstitute to whole basis before analysis. See 143.12b for reporting results on concentrates and dehydrated products. Prepare low fat dairy products (e.g., skim milk, buttermilk, nonfat dried milk and uncreamed cottage cheese) on an "as is" basis. See 143.12a for reporting results on low fat dairy products.

(2) Specific Product Preparation - Special preparation is specified for certain processed foods in 141.22b.

141.21 Guide to Determining How to Prepare Processed Foods. Determine the type of sample and reasons for analysis. Use the preparation procedure for that type sample.

Sample Type	Criteria	Procedure
I-P	Meets ALL the following criteria: (a) Collected for multi residue determination (b) No background information or background information does not indicate likelihood of contamination by specific pesticide or industrial chemical.	Consult 141.22b and if product is listed there, prepare as directed; if not listed, prepare the "as is" product as received or as introduced into interstate commerce.
II-P	Meets ANY of the following criteria: (a) Selectively collected for particular residue(s) (b) Selectively collected because of suspected likelihood of particular residue. (c) Collected from an area where a known residue problem exists. (d) Analysis of a type I-P sample reveals a significant residue for which a tolerance is established on the product analyzed.	Consult the specific tolerance regulations listed in 21 CFR 121 or 21 CFR 122 for preparation that may be required by regulation. If no tolerance is established for the residue in the particular processed food, the analyst must decide, based on the particular circumstances, how best to prepare sample.

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77-1 (03/01/77)

SAMPLE COMPOSITING

Composite prepared sample according to guidelines in 142.2 by chopping, grinding, blending, etc. to obtain homogeneous mixture. The relatively small portion (25-100 g) of prepared composite that is taken for analysis must be representative of gross laboratory sample. Routine chopping, grinding, blending, etc. does not always produce a proper homogenate, as is the case with dried hays and some fish samples. When product is not visibly homogeneous, use standard mixing and quartering techniques to insure that portion for analysis is representative. See 142.4 for notes on preparing composites for analysis. Select representative portion of uniformly mixed sample for analysis.

142.1 Portion of Sample for Dithiocarbamate Analysis. Some dithiocarbamate compounds decompose rapidly in presence of slurry of crop material. Cullen (Anal. Chem, 36, 221-224 (1964)) reported that speed is essential as soon as surface of crop is broken and dithiocarbamate is in intimate contact with water, enzymes, and sugars. He noted a rapid decrease in recovery with time of contact in aqueous crop solution and recommended that samples for dithiocarbamate analysis be either analyzed immediately after harvest or frozen for storage.

When dithiocarbamate residues are to be determined, select representative units for dithiocarbamate analysis prior to chopping, grinding or blending sample. Where sample units are small and free flowing (e.g. grains, beans, berries, etc.), mix well and take whole units for analysis; where sample units are large, take wedges from each unit. Analyze immediately or freeze immediately after cutting. An exception to above is where commodity contains free juices (e.g. tomatoes, apples, oranges, etc.) and requires cutting in pieces to fit into apparatus. In such cases, take representative whole units and freeze before cutting. Dice frozen units without allowing them to thaw; mix and take sample for analysis.

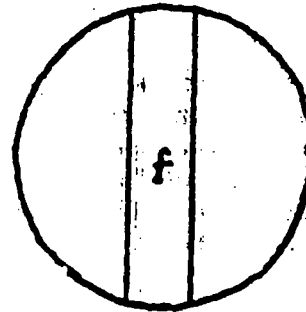
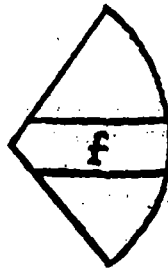
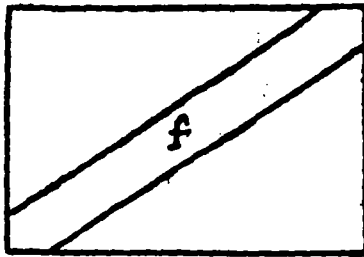
142.2 Guidelines for Preparation of Composites.

142.21 Total Sample Composited and Comminuted. Where practical, comminute and thoroughly mix entire prepared sample. See 142.1 for portion to be removed if sample is to be analyzed for dithiocarbamates.

142.22 Total Sample Composited and Fraction of Sample Comminuted.

142.22a Product with Small Units. Where sample product consists of small units (e.g., grains, cherries, nuts, dried peas and beans) and it is not practical to prepare and comminute entire sample, mix and quarter down to approximately 4 pounds or 4 quarts. From quartered sample, prepare product as in 141.1 or 141.2 and chop or grind prepared sample to obtain minimum of 1 pound or 1 quart comminuted sample for original analysis. See 142.4(4) for grinding low moisture products.

142.22b Product of Homogeneous Nature. Where large sample of homogeneous nature must be composited (e.g., butter, cheese), and melting entire sample of butter or dicing, shredding, or blending entire sample of cheese is not practical, prepare sample for original analysis by taking equal portions from each packaged unit. Where large blocks, wedges or wheels of cheese are to be prepared, take fraction (f) for analysis as in diagram below.



Prepare cheese as in 141.22b(2) and composite by dicing, shredding or blending.

142.23 Composite of Individual Subdivisions. Where identity of subdivisions must be maintained for possible additional analysis of individual subs, prepare composite as follows:

- | | |
|--------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| (1) Animal tissue | Grind each sub (meat grinder). Composite 100 g from each sub and grind again. |
| (2) Dairy products | Equal weight from each sub. Grind, dice or blend. |
| (3) Eggs | Half of eggs in each sub. Blend. See 142.4(2). |
| (4) Feed, forage and hay | Quarter each sub down to 200 g (100 g for processed feeds and silage). Composite 200 (100) g from each sub. Chop or grind to pass 20 mesh. See 142.4(4). |
| (5) Fruits | (a) Large (apples, pears, tomatoes, etc.): sample each unit within sub. Composite an equal weight from each sub. Chop or blend.
(b) Small: 200 g from each sub. Chop or blend. |
| (6) Grains | 100 g from each sub after thorough mixing. Grind composite to pass 20 mesh. See 142.4(4). |
| (7) Milk | 100 g (ml) from each sub after thorough mixing. |
| (8) Nuts | Remove and discard shells. Composite equal weight, 100 g or more, of nut meats from each sub. Chop or grind. |
| (9) Pod Vegetables | (Beans, peas, etc., also asparagus) 200 g from each sub after thorough mixing. Chop or grind. |

- (10) Root Vegetables Sample each unit within sub taking equal weight from each sub. Chop or grind.
- (11) Seeds 100 g from each sub after thorough mixing. Grind composite to pass 20 mesh. See 142.4(4).
- (12) Spices 200 g from each sub after thorough mixing. Grind or chop.
- (13) Stalk Vegetables (Celery, broccoli, etc.). Quarter each stalk in sub lengthwise. Take two opposite quarters from each stalk and composite these quarters by chopping.
- (14) Vegetables (a) Head: quarter each head in sub. Take two opposite quarters from each head and composite these quarters by chopping.
- (b) Leafy
- (1) Leaf cut: mix sub well and select leaves at random until 200 g portion is obtained. Composite 200 g from each sub and chop entire composite.
- (2) Field cut (leaves attached to stalk): select bunches at random until 500 g portion is obtained. Composite 500 g from each sub and chop entire composite.

142.3 Portions of sample retained. Select three portions from total sample homogenate (142.21) and identify one as "original analysis", second as "check analysis", and third as "reserve" (for claimant.) Where fraction sample composites (142.22) and individual sub composites (142.23) have been prepared, retain prepared composite and reserve of sample. Seal and store all retained portions of sample in such manner as to prevent decomposition of product and residue. This requires that all products be frozen until findings of original analysis have been verified. The amount of composite retained is governed by extent of analysis required on sample. However, in no case should portions be less than one quart each (or for products of high density, one pound) for original, check, and reserve. Sample size for analysis is given in method.

142.4 Notes on compositing and comminuting.

(1) Using Hobart vertical cutter mixer. The 40 quart Hobart vertical cutter mixer was tested to determine its mixing and chopping ability. Varying quantities of several agricultural products were chopped for varying time intervals and resulting mixtures were checked for distribution and particle size. Based on this study, a minimum of 20 lbs. of compactly formed products (such as potatoes, beets, carrots, etc.) or a minimum of 1/2 bushel of loosely formed products (such as cabbage, lettuce, greens, etc.) is recommended for chopping composite in 40 quart Hobart vertical cutter mixer. Chop a minimum of five (5) min, stopping chopper and hand scraping material back into bottom

of chopper at least once during operation. (More, C.A., private communication, Food and Drug Adm., June, 1966).

(2) Blending eggs. Blend at low speed for minimum of five (5) min or until sample is homogeneous. Low speed blending will minimize foaming or "whipping" of sample.

(3) Thawing frozen composites. Thaw frozen composites completely and remix before portion is taken for analysis. Any liquid phase separation that occurs in freezing or thawing must be reincorporated into composite before taking sample for analysis.

* (4) Grinding low moisture products, oilseeds, and other difficult samples. Grind samples to fine mesh (ca 20 mesh) in Ultra Centrifugal Mill (see 111) or equiv. Grind oil seeds first through a large sieve (3-5 mm), then regrind through a fine (<0.5 mm) sieve to minimize drag on the motor. Collect ground material in the 500-800 g capacity collecting pan and thoroughly mix several batches as necessary to provide appropriate sample size from which to take the analytical sample. (Sawyer, L.D., private communication, Food and Drug Admin., Jan., 1977.)

In the absence of a centrifugal mill, grind samples through a Wiley mill or equiv., taking care to prevent physical separation of the product in the mill. A stepwise grinding procedure, in which sample is coarsely ground, then quartered down and a smaller portion ground to 20 mesh or smaller, may be necessary with some products. Loss of volatile pesticides can occur during grinding where heat is generated in process. Dry Ice has been used to precool mills before sample is ground.

It may also be advisable to grind materials such as hay through the Wiley mill prior to final grinding through the centrifugal mill.

* (5) Grinding of fish. To prevent the skin of fish from clogging the grinder during the preparation of fish samples, the fish may be frozen prior to grinding. Sample handling must be consistent with the directions given in 141.12c and 141.22b, in terms of the portion of the sample retained for analysis. A distinction must be made between (1) fish frozen by a processor for sale as frozen fish and (2) raw fish sampled by an inspector and frozen for preservation prior to analysis. In the former situation, the sample must be thawed and the drainings discarded, no matter what further handling is required for analytical sample preparation. In the latter case, no drainings should be discarded and fish need be thawed only enough to facilitate preparation of the analytical samples.

Prepare raw fish (or fish sampled raw and frozen by the inspector) as described in 141.12c, then freeze in portions of suitable size for introduction into the grinder.

Thaw frozen fillets and discard drainings as described in 141.22b. Then refreeze in portions of suitable size for introduction into the grinder.

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Thaw whole fish frozen for sale as frozen fish and discard drainings, then prepare as described in 141.22b. Refreeze in portions of suitable size for introduction into the grinder. Grind immediately three times in a Hobart Food Cutter (or equiv.) with grinder attachment. (Thompson, T.D., private communication, Food and Drug Admin., Feb., 1976).

ATTACHMENT 4

SAMPLING EQUIPMENT

CRAB ORCHARD NATIONAL WILDLIFE REFUGE

SAMPLING EQUIPMENT

PHASE I & II SAMPLING

NUMBER or AMOUNT

per UNIT (person, NUMBER OF TOTAL NO. WHERE AVAILABLE
site, or sample) X UNITS = NEEDED (here, St. Louis, etc.)

HIT LIST (sub.1)

SAMPLING EQUIPMENT:

SITE IDENTIFICATION:

2"x2"x24" wooden stakes.....	100	-	100
orange spray paint.....	2 cans	-	2
rope.....	400 ft.	-	400 ft
hammer.....	1	-	1

WATER:

vaders.....	2size10; 2size12		4
boat.....	1	-	1
disposable stirrers.....			
2" submersible pump.....			
water filtering device.....			
filters.....			
100 ft. steel tape.....			
shovel.....			
electrical cord.....			
glass funnel.....			
deep buckets.....			
paper towels.....			
plastic sheeting.....	10'x50'roll	2	2 rolls
polypropylene rope.....			
silicone spray.....			
flagging tape.....			
electrical tape.....			
aluminum foil.....	3 rolls		3 rolls
tool kit: phillipshead screwdrivers.....	3 sizes		3
wrenches.....	2 crescent; 2 pipe		4
hammers.....	(1) 5#; (1) 1# claw		2
knife.....	1		1
pliers.....	1 ndle-nose; 1 reg.		2
tubing bender.....	(1) 3/8"		1
tubing cutter.....	1		1
saw.....	1		1

? automatic cord reeler and lead cord.....

SEDIMENT:

aluminum pans.....	1 dozen		
Wildco hand operated core sampler.....			
2"OD, 1/16" thickness Lexan tubing.....	8 foot lengths	25	200 ft
polypropylene scoops.....	6		
aluminum scoops.....	6		
disposable spatulas.....			

GEOPHYSICAL:

pH meters.....			
specific conductance meters.....			
thermometers.....			
magnetometer/electromagnetic induction equipment...			
surveying equipment.....			
water level probe.....	1		1
[sampling trier.....			
[soil auger.....			
[split barrel sampler.....			

CRAB ORCHARD NATIONAL WILDLIFE REFUGE SAMPLING EQUIPMENT

PHASE I & II SAMPLING

HIT LIST (sub.1)

NUMBER or AMOUNT
per UNIT (person, NUMBER OF TOTAL NO. WHERE AVAILABLE
site, or sample) X UNITS = NEEDED (here, St. Louis, etc.)

coolers.....	(10) 20 quart	10
sampler jars (see BOTTLES file).....		
freezer.....	1	1
van with roof rack.....	1	1
dry ice.....		
ice.....		
shipping labels.....		
markers.....		

DOCUMENTATION:

field notebooks.....		
sample tags.....		
record sheets.....		
chain-of-custody records.....		
camera.....	1	1
35 mm, color slide film.....		

QA/QC:

field blanks.....		
duplicate samples.....		
split samples.....		
ignitability field test.....		

SAFETY EQUIPMENT:

GENERAL PERSONAL GEAR (SAFETY LEVELS B, C, AND D):

- calibrated HNU-1101 photoionizing air monitor.....
- pressure demand self-contained breathing apparatus;
high efficiency organic vapor/particulate/pesti-
cide cartridge (respiratory safety level C).....
- rubber safety boots or safety workboots with rubber
overboots (safety levels B, C, & D).....
- cotton overalls (level D) or work clothing under
white tyvek suit (levels B & C).....
- tyvek or other hood (levels B & C).....
- cotton gloves (level D) or surgeon's gloves with
rubber overgloves (levels B & C).....
- protective eyewear.....
- hard hat (during drilling).....
- noise protection (during drilling).....
- 2 way communication.....
- chemical resistant clothing (yellow tyveks, PVC cover-
alls, or butyl apron) as needed for specific
tasks.....
- first aid kit and manual.....

LEVEL A-HIGHEST LEVEL OF RESPIRATORY, SKIN, AND EYE PROTECTION:

THE ABOVE LIST PLUS:*

- chemical-resistant fully encapsulating suit.....
- chemical-resistant outer and inner gloves.....
- chemical-resistant boots with steel toe and shank..
- disposable protective suit, gloves, and boots (worn
over fully encapsulating suit).....

LEVEL B:

THE GENERAL GEAR LIST PLUS:*

- chemical-resistant clothing (overalls and long-

SAMPLING EQUIPMENT

PHASE I & II SAMPLING

NUMBER or AMOUNT

per UNIT (person, NUMBER OF TOTAL NO. WHERE AVAILABLE
site, or sample) X UNITS = NEEDED (here, St. Louis, etc.)

HIT LIST (sub.1)

sleeved jacket; coveralls; hooded, one or two-
piece chemical-resistant splash suit; disposable
chemical-resistant coveralls).....
chemical-resistant outer and inner gloves.....
chemical-resistant boots with steel toe and shank..
chemical-resistant disposable outer boots.....
hard-hat with face shield.....

LEVEL C:

THE GENERAL GEAR LIST PLUS:*

chemical-resistant clothing (coveralls; hooded, two-
piece chemical-resistant splash suit; chemical-
resistant hood and apron; disposable, chemical-
resistant coveralls).....
chemical-resistant outer and inner gloves.....
chemical-resistant boots with steel toe and shank..
chemical-resistant disposable outer boots.....
hard-hat with face shield.....
escape mask.....

LEVEL D:

THE GENERAL GEAR LIST PLUS:*

boots/shoes: leather or chemical-resistant with
steel toe and shank.....
chemical-resistant disposable outer boots.....
hard hat with face shield.....
escape mask.....
safety glasses or chemical splash goggles.....

*MAY INCLUDE MORE SPECIFIC DESCRIPTIONS OF SOME GENERAL LIST ITEMS)

NOTE: Level B protection should be available in the event that the nature
and hazards of a site are unknown, and must be further defined by on-
site studies. Safety levels can later be modified appropriately.

DECONTAMINATION:

brushes.....	6	6
tub.....		
acetone.....	1 gal	1 gal
hexane.....	1 gal	1 gal
distilled water.....	5 gal	5 gal
55 gallon drums.....	4	4
interference-free, redistilled solvent (eg. acetone or methyl chloride).....		
detergent.....		
5 gallon pails.....		
kiddie pool.....	2	2
Gateraid.....	2 cases	2 cases
fire extinguishers.....	1 ABC	1
Jerry jugs.....	(4) 5 gal	4
plant sprayer.....	1 10 gal	1
air horns.....	2	2
plastic garbage cans.....	2	2
scissors.....	2 pair	2 pair
pocket knives.....	3	3
Janitor-in-a-drum cleaner.....	1	1

amount	SYRACUSE	check	amount	St. LOUIS	check	amount	REFUGE/MARION	check
	LAB			VAN WITH ROOF RACK			BOAT (REFUGE)	
	-----						ICE (MARION)	
	SAMPLING JARS (see pages 2&3)			DRY ICE			DISTILLED WATER	
	RECORD SHEETS			COOLERS			(EITHER AT AN INDUSTRY)	
	CHAIN-OF-CUSTODY RECORDS			ALUMINUM PANS			OR FROM SOUTHERN	
	DETERGENT			PLASTIC PAILS			ILLINOIS UNIVERSITY)	
	SOLVENT (NANO GRADE):			WADERS			FREEZER	
	ACETONE			TOILET BRUSHES			STATION WAGON	
	HEXANE			KIDS POOL				
	WATER FILTERING DEVICE			GATERAID				
	FILTERS			FIRE EXTINGUISHER				
	DETERGENT			JERRY JUGS				
	-----			PLANT SPRAYER				
	HYDROGEOLOGIC			PLASTIC SHEETING				
	-----			AIR HORNS				
	WATER LEVEL PROBE			GARBAGE CANS				
	ELECTROMAGNETIC EQUIP'T			SCISSORS				
	SURVEY EQUIPMENT			POCKET KNIVES				
	-----			JANITOR-IN-A-DRUM				
	SUPPLY			ALUMINUM SCOOPS				
	-----			POLYPROPYLENE SCOOPS				
	SHIPPING LABELS			LEXAN TUBING				
	MARKERS			ROPE				
	I.D. STICKERS (RED & YELLOW)			HAMMER				
	RUBBER BANDS			STAKES				
	FOLDERS			ORANGE PAINT				
	-----			ALUMINUM FOIL				
	DIV. 3			HACKSAW				
	-----			100 ft. STEEL TAPE				
	CAMERA			SHOVEL				
	COMPUTER SAMPLE LABELS			ELECTRICAL CORD				
	pH METER			GLASS FUNNEL				
	SPEC. CONDUCTANCE METER			DEEP BUCKETS				
	SAFETY EQUIPMENT (see page 4)			PAPER TOWELS				
	-----			POLYPROPYLENE ROPE				
				SILICONE SPRAY				
				FLAGGING TAPE				
				ELECTRICAL TAPE				
				DISPOSABLE SPATULAS				
				DISPOSABLE STIRRERS				
				THERMOMETERS				
				DRUMS				
				SQUEEZE BOTTLES				
				TUB				
				INTERFERENCE-FREE				
				REDISTILLED SOLVENT				
